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ON THE

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ON THE

PROGRESS OF CHEMISTRY

FOR 1924.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society, or issued by the Bureau of Chemical Abstracts.*
Amer. J. Bot.	American Journal of Botany.
Amer. J. Hygiene	American Journal of Hygiene.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Report	Annual Reports of the Chemical Society.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Néerland. physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Sächs. Akad. Wiss.	Berichte uber die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Brennstoff-Chem.	Brennstoff Chemie.
Brit. Med. J.	British Medical Journal.
Bul. Soc. Chim. România	Bulétinul Societătei de Chimie din România.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Chem. and Ind.	Chemistry and Industry.

* The year is not inserted in references to 1924.

Abbreviated Title.	Journal.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Védu a Průmysl."
Chem. News	Chemical News.
Chem. Umschau	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad	Chemisch Weekblad.
Chem. Ztg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Helv. Chim. Acta	Helvetica Chimica Acta.
J.	Journal of the Chemical Society.
Jahrb. Radioaktiv. Electronik	Jahrbuch der Radioaktivität und Elektronik.
Japan. J. Chem.	Japanese Journal of Chemistry.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Ind. Japan	Journal of Chemical Industry, Japan.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
J. Chim. phys.	Journal de Chimie physique.
J. Exper. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan.	Journal of the Pharmaceutical Society of Japan.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Phys. Radium	Journal de Physique et le Radium.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Kolloid Z.	Kolloid Zeitschrift.
Landw. Versuchs-Stat.	Die Landwirtschaftlichen Versuchs-Stationen.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres	Mémorial des Poudres.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nach. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss	Die Naturwissenschaften.
Oesterr. Chem.-Ztg.	Oesterreichische Chemiker-Zeitung.
P.	Proceedings of the Chemical Society.
Papierfabr.	Papier-Fabrikant.

Abbreviated Title.	Journal.
Pflüger's Archiv.	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society of Experimental Biology and Medicine.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell'Academia delle Scienze Fisiche e Matematiche Napoli.
Rev. gén. Bot.	Revue générale de Botanique.
Rev. gén. Coll.	Revue générale des Colloïdes.
Sci. Rep. Tohoku Imp. Univ.	Science Reports, Tohoku Imperial University.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften Wien.
Soil Sci.	Soil Science.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. deut. Oel-Fett. Ind.	Zeitschrift der deutschen Oel- und Fett-Industrie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. Nahr.-Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE maintenance of steady progress in the investigation of physico-chemical problems is indicated by the output of research during the current year. The choice of material for report and discussion in this particular section is to some extent restricted by the circumstance that colloid chemistry and subatomic phenomena are to form the subjects of special reports which will appear in this volume.

The topics selected include surface energy, rotatory dispersion, mechanism of reactions, and electrode phenomena. A brief and admittedly very inadequate account is also given of some of the recent developments which are intimately bound up with the interpretation of the properties of solutions of electrolytes.

The Scattering of X-Rays.

The remarkable success achieved by the quantum theory in its application to the Bohr atom and in the quantitative interpretation which the Einstein equation affords of the phenomena associated with the transformation of radiant energy into kinetic energy, whether the radiant energy is of the comparatively long-waved infra-red type, of the intermediate type belonging to the field of optics, or of the very short-waved *X*-ray type, represents one of the chief advances which have yet been made in the interpretation of physical phenomena. These successes might warrant the belief that the assumed energy quanta are real entities, were it not for the difficulty which this view meets with in the explanation of interference phenomena.

In a recent paper, A. H. Compton [1] describes observations which are said to justify the opinion [2] that the scattering of *X*-rays by electrons is also a quantum phenomenon, although such scattering has usually been regarded as a phenomenon, the interpretation of which is to be sought in terms of the classical theory.

[1] *Physical Rev.*, 1923, **21**, 483; 1923, **22**, 409.

[2] P. Debye, *Physikal. Z.*, 1923, **24**, 161.

On the assumption that the impact between an X-ray quantum and an electron is a process to which the laws of conservation of energy and momentum apply, and that the energy exchange is confined to a single electron, it is possible to calculate the resulting alteration in the wave-length of the X-ray. Experiments made with homogeneous molybdenum X-rays scattered by carbon show a change in wave-length which agrees closely with the predicted amount. Although some doubt has been thrown on the interpretation of the results, the experimental observations have been confirmed,[3] and by further independent measurements,[4] in which the X-rays have been scattered by other elements, the Compton-Debye effect seems to have been definitely established. It is stated [5] that the effect is not observable with the heavier elements.

These observations are of importance in that they extend the experimental support for the validity of the Einstein equation into an entirely new region. Not only so, but it has been argued with some justification that the Compton-Debye effect affords substantial evidence for the reality of the discrete energy quanta postulated by Planck and by J. J. Thomson.

Observations [6] on the scattering of γ-rays by different elements have also been found to be in qualitative agreement with the distribution formula derived by Compton. Compared with experiment, the formula for mono-electronic quantum scattering gives, however, lower values for the total scattering absorption and much lower values for the relative scattering.

The electrons generated by the passage of γ-rays through gases contained in a Wilson cloud chamber are found [7] to have velocities corresponding with paths of about 1 cm. These velocities are much less than those which the electrons would attain if a complete quantum of γ-radiation were absorbed, and the facts are considered to be in favour of the theory of scattering suggested by Compton and Debye.

Rotatory Dispersion and Chemical Constitution.

Some ten years ago, an attempt was made to systematise our knowledge of the rotatory dispersion of organic compounds on the basis of Drude's electronic formula, $\alpha = \Sigma k_n/\lambda^2 - \lambda_n^2$. According to the proposals put forward by Lowry and Dickson,[8] the dispersion is " simple " if it can be expressed by a single term of this formula,

[3] P. A. Ross, *Proc. Nat. Acad.*, 1923, **9**, 246.
[4] J. A. Becker, *ibid.*, 1924, **10**, 342. M. de Broglie and A. Dauvillier, *Compt. rend.*, 1924, **178**, 908, 2076; **179**, 11; *A.*, ii, 581.
[5] A. Dauvillier, *Compt. rend.*, 1924, **178**, 2076; *A.*, ii, 645.
[6] N. Ahmad and E. C. Stoner, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 8; *A.*, ii, 582.
[7] D. Skobelzyn, *Z. Physik*, 1924, **24**, 393; *A.*, ii, 582.
[8] *J.*, 1913, **103**, 1067.

but is " complex " if two (or more) terms are required. The method commonly employed in practice for distinguishing between these two types consists in plotting $1/\alpha$ (the reciprocal of the observed rotation) against λ^2 (the square of the wave-length of the light employed). A straight-line graph has been held to indicate " simple " dispersion. The nature of the deviations, whether systematic or accidental, which is found on comparison of the observed rotations with those calculated from the assumed dispersion formula affords an obvious alternative method for testing the character of the rotation dispersion.

Recent observations show clearly, however, that linearity of the $1/\alpha$–λ^2 graph over the measured range of wave-lengths cannot by any means be regarded as conclusive proof that the dispersion of a particular substance is of the single-term type. The rotation data [9] for the normal aliphatic ethers of *d*-γ-nonanol yield values for the dispersion ratio $\alpha_{4358}/\alpha_{5461}$ which, for the most part, lie between 1·40 and 1·50. This ratio, according to the one-term formula, is equal to $(0{\cdot}5461^2-\lambda_0^2)/(0{\cdot}4358^2-\lambda_0^2)$, and this has a minimum value (when $\lambda_0 = 0$) equal to 1·57. The representation of the apparently simple rotatory dispersion of these esters would therefore seem to require two or more terms of the Drude formula.

That the straight-line graph does not afford a means of distinguishing between " simple " and " complex " dispersion has also been demonstrated in a general manner by H. Hunter.[10] Analysis of the two-term formula $\alpha = k_0/(\lambda^2 - \lambda_0^2) + k_1/(\lambda^2 - \lambda_1^2)$ leads to the conclusion that in practice it will be impossible to detect the departure of the $1/\alpha$–λ^2 curve from linearity when k_0 and k_1 are both positive. If the rotation constants are of opposite sign and if $k_0 > k_1$ when $\lambda_0 > \lambda_1$, detection will be possible only in very rare cases. The only condition under which the experimental data can be expected to show the effect which Lowry and Dickson regard as evidence of " complex " dispersion is when the rotation constants are opposite in sign and $k_0 < k_1$ when $\lambda_0 > \lambda_1$.

Quite apart from the fact that there is no evidence to justify the assumption that the rotatory dispersion of organic compounds is ever controlled by a single absorption band, the above considerations lead to the conclusion that the grouping proposed by Lowry and Dickson is inadmissible on practical grounds and that a return to the older classification, which distinguishes between normal and anomalous dispersion, is desirable. If the alternative grouping is retained, the distinction should be between rotatory dispersion which is " apparently simple " and that which is " obviously com-

[9] J. Kenyon and T. W. Barnes, *J.*, 1924, **125**, 1395.
[10] *Ibid.*, p. 1198.

plex." [11] At the best, such a classification would be empirical, and could scarcely be regarded as a satisfactory method for the derivation of numbers which are to be used for the comparison of the rotatory powers of different substances, for these numbers, although free from the influence of dispersion, would still be empirical in character.

In view of the difficulties which are met with in compounds which contain a single asymmetric carbon atom, it would seem futile at present to attempt to trace any connexion between the theory underlying the Drude equation and the rotation data for compounds which contain more than one asymmetric carbon atom. For such compounds, the representation of the connexion between rotation and wave-length is necessarily empirical for the present.

According to Lowry and Richards,[12] the dispersion of sucrose in aqueous solution (260 g. per litre at 20°) can be represented by the two-constant formula $[\alpha] = 21{\cdot}648/(\lambda^2 - 0{\cdot}0213)$, in which the dispersion constant is of similar magnitude to those obtained for the simple secondary alcohols. Since sucrose contains nine asymmetric carbon atoms of the same type, it is suggested that the several partial rotations are controlled by dispersion constants which are either identical or so nearly equal that the corresponding absorption bands would be indistinguishable. This may well be the case, but for such compounds the rotation dispersion cannot at present be described otherwise than as " apparently simple."

The question whether anomalous dispersion (actual or potential) can always be interpreted in terms of the relations between the rotation and dispersion constants of the Drude formula is of considerable importance. Substances are known [13] the dispersion of which is normal at one temperature and anomalous at another. This may be due to an alteration in the relative values of the rotation constants, such that k_0/k_1 is greater than, equal to, or less than unity, according to the temperature. Such an interpretation implies chemical homogeneity of the molecules, and is in a certain sense directly opposed to the widely accepted view that anomalous dispersion is to be attributed to the superposition of the rotations of two (or more) kinds of molecules in the substance concerned.

According to W. T. Astbury,[14] the anomalous rotatory dispersion of crystalline tartaric acid is the combined result of the dextrorotation of the individual molecules of the acid and a lævorotation which has its origin in the spiral arrangement of contiguous

[11] H. Hunter, *J.*, 1924, **125**, 1389.
[12] *Ibid.*, p. 2511.
[13] C. E. Wood and M. A. Comley, *ibid.*, p. 2630.
[14] *Proc. Roy. Soc.*, 1923, [*A*], **102**, 506.

hydroxyl groups belonging to adjacent molecules. This explanation is not confined to the solid state, for Astbury interprets the anomalous dispersion of solutions of tartaric acid in the same way by assuming that such solutions contain complex groups of tartaric acid molecules in which the spiral disposition of the hydroxyl groups is maintained. This hypothesis would be difficult to reconcile with the osmotic and conductivity data for such solutions, and is inconsistent with observations [15] which have been made on solutions of ethyl tartrate. The anomalous dispersion of the ester, dissolved in various solvents to give solutions of varying concentration, bears no obvious relation to the molecular condition of the ester indicated by freezing-point measurements.

Whilst this particular hypothesis thus readily admits of direct experimental test, the more subtle assumption of dynamic isomerism as the cause of anomalous rotatory dispersion has in this respect an obvious advantage.

In view of what has been stated, the postulation of dynamic isomerism as the cause of optical heterogeneity would seem to necessitate the conclusion that chemical heterogeneity is by no means limited to substances which belong to any particular chemical group. For many such substances—for example, the ethers of *d*-γ-nonanol referred to in a preceding paragraph—the assumption of dynamic isomerides would conflict with the chemical evidence, and any attempt to explain the optical properties in terms of dissociation or association would be equally incompatible with known facts.

Surface Energy.

The large amount of experimental work which has been carried out in recent years with a view to the elucidation of the nature and properties of surface films and boundary layers has directed renewed attention to some of the older problems connected with the surface energy of liquids. In this connexion, many attempts have been made to ascertain the dependence of surface tension on temperature and to establish a relation between the surface tension and the densities of the co-existing liquid and vapour phases.

In addition to the well-known formula of Eötvös-Ramsay-Shields and the much less familiar formula derived by van der Waals, both of which may be said to have a theoretical basis in the ideas underlying the reduced equation of condition and the theory of corresponding states, numbers of equations have been put forward which are entirely empirical in origin. The latter have, in some cases, considerable practical value, but apart from this, it may be

[15] T. M. Lowry and J. O. Cutter, *J.*, 1924, **125**, 1465.

said that the chief interest which attaches to these empirical formulæ is the possibility of tracing a connexion between them and the formulæ which have an accepted theoretical basis.

The type of formula which is of most interest is that represented by

$$\gamma = K(D - d)^p(1 - T_r)^q \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which γ is the surface tension, T_r the reduced temperature, D and d are the densities of the liquid and saturated vapour respectively, and K, p and q are constants. In the formulæ of this type, p and q are positive quantities, but either of them may be equal to zero, in which case the general formula assumes the form

$$\gamma = K(D - d)^p \text{ or } \gamma = K(1 - T_r)^q.$$

At temperatures sufficiently far removed from the critical temperature, d may, of course, be neglected in comparison with D with a corresponding increase in the simplicity of the equation.

A formula of the general type is that recently put forward by W. L. Levschin,[16] who, by reference to the surface tension measurements of Ramsay and Shields and the density measurements of Young, and by use of the method of least squares, finds that the relation $\gamma = K(D - d)^{2\cdot36}(1 - T_r)^{0\cdot5}$ affords a satisfactory account of the experimental data.

The Eötvös formula is of this type in that it may be written $\gamma = KD^{2/3}(1 - T_r)$, where K is a specific constant dependent on the molecular weight of the liquid. As is well known, the above relation fails to give an account of the experimental data at higher temperatures, and in this respect is less satisfactory than the modified equation, suggested by M. Katayama,[17] which may be written

$$\gamma = K(D - d)^{2/3}(1 - T_r) \quad . \quad . \quad . \quad . \quad (2)$$

The equations derived by van der Waals [18] which give the relation between the surface tension and the temperature are

$$\gamma = K_1T_cV_c^{-2/3}(1 - T_r)^q \text{ and } \gamma = K_2T_c^{1/3}p_c^{2/3}(1 - T_r)^q \quad . \quad . \quad (3)$$

in which T_c, V_c, and p_c are the critical data and K_1, K_2, and q are universal constants.

These equations in the form

$$\gamma = \gamma_0(1 - T_r)^q \quad . \quad . \quad . \quad . \quad . \quad (4)$$

have been found [19] to represent satisfactorily the behaviour of non-associated liquids when q is varied between narrow limits.

[16] *Z. physikal. Chem.*, 1924, **112**, 167; *A.*, ii, 829.
[17] *Sci. Rep. Tohoku Imp. Univ.*, 1916, **4**, 373; *A.*, 1916, ii, 219.
[18] *Z. physikal. Chem.*, 1894, **13**, 716.
[19] A. Ferguson, *Phil. Mag.*, 1916, [vi], **31**, 37; *A.*, 1916, ii, 174.

More recently, it has been shown that the connexion between the surface tension and the orthobaric densities D and d may be expressed very exactly by the equation [20]

$$\gamma = K(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

over a temperature range which extends to within about 40° of the critical temperature.

By combination of (2) and (5) the density term in the equation of Katayama may be eliminated, leading to

$$\gamma = \gamma_0(1 - T_r)^{1\cdot20} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

a result which, in so far as it indicates that the exponent q in equations (3) and (4) has the same value for all liquids, is in complete agreement with the conclusion drawn by van der Waals on theoretical grounds.

Equation (6) has been tested by S. Sugden,[21] who, by using the best available data, finds that this equation reproduces with great accuracy the connexion between surface tension and temperature, even when the latter approaches close to the critical temperature, provided that the liquids in question are non-associated. For such liquids, the values of the constants K_1 and K_2 in equation (3) are also found to be approximately independent of the nature of the substance.

In the comparison of the surface energies for different liquids, some authors have preferred to make use of the total surface energy on the ground that this is independent of the temperature. The connexion between the total (λ) and free (γ) surface energies is given by $\lambda = \gamma - Td\gamma/dT$. By substituting in this the value of γ given by equation (6), the relation

$$\lambda = \gamma_0(1 + 0\cdot2T_r)(1 - T_r)^{0\cdot2} \quad . \quad . \quad . \quad . \quad (7)$$

is obtained.[22] From this it appears that at corresponding temperatures the total surface energies are proportional to the values of γ_0.

According to views which have been put forward by Langmuir [23] and by Harkins,[24] the molecules in the surface layer are oriented,

[20] D. B. Macleod, *Trans. Faraday Soc.*, 1923, **19**, 38; compare also A. Batschinski, *Irw. fiz. Inst. Moskow Naucnom Inst.*, 1922, and *Trans. Faraday Soc.*, 1924, **20**, 211. According to G. N. Antonov, *Z. physikal. Chem.*, 1924, **112**, 461, the graph obtained by plotting γ against $(D - d)$ is discontinuous. It is probable, however, that the discontinuity is to be attributed to errors of experiment in the measurement of the quantities involved.

[21] *J.*, 1924, **125**, 32.

[22] *Idem, ibid.*, p. 1167.

[23] *J. Amer. Chem. Soc.*, 1917, **39**, 1848.

[24] W. D. Harkins, E. C. H. Davies, and G. L. Clark, *ibid.*, p. 541; *A.*, 1917, ii, 239.

and the total surface energy is determined by the atoms or groups which are farthest from the liquid surface. If this view is correct, it would seem to follow that regularities should be evident in the total surface energies of comparable compounds. Such a group of comparable substances is afforded by the unsymmetrical *p*-disubstitution products of benzene, the molecules of which are supposed to be oriented with the para-axis normal to the surface of the liquid and to occupy the same area in the surface. The examination of a number of such compounds by Sugden [25] affords no evidence of the existence of such regularities in the values of γ_0, and the conclusion is drawn that if the surface molecules have a definite orientation, the total surface energy cannot be determined by the groups which are directed outwards, but is dependent on the nature of the molecule as a whole.

A novel method of comparing molecular volumes based on Macleod's surface tension–density rule has been suggested and examined by Sugden.[26] If the fourth root of the specific constant, K, in equation (5) above is multiplied by the molecular weight, M, a quantity, P, is obtained which may be written

$$P = M\sqrt[4]{K} = \frac{M}{D-d}\gamma^{1/4}.$$

At low temperatures, $M/D - d$ represents the molecular volume, and the values of P, which is termed the *parachor*, afford a comparison of the molecular volumes of liquids at temperatures at which the surface tensions have the same value. On the assumption that the magnitude of the surface tension may be regarded as a measure of the internal pressure, Sugden's method renders it possible to compare the molecular volumes at one and the same value of the internal pressure.

It has been found that the parachor is an additive quantity which can be reproduced by adding together two sets of constants, one of which represents the contribution of the atoms present in the molecule of the compound, whilst the other represents the influence of constitutional factors. The atomic and structural parachors show a degree of constancy which is very distinctly in favour of Sugden's method as compared with that followed in the molecular volume systems of Kopp and Le Bas. In all, 167 compounds have been examined and for 145 of these the calculated parachors are within 2% of the observed values; for 104, the difference in question is less than 1%.

In support of the view that the parachor is a correct measure of the molecular volume, it is found that P bears an approximately

[25] *Loc. cit.* [26] *J.*, 1924, **125**, 1177.

constant ratio to the critical volume; the equation $P = 0{\cdot}78\ V_c$ gives critical volumes which differ from the accepted values by less than 3%.

In reference to the abnormally large values [27] (4 to 5·5) given for the Eötvös coefficient by certain substances, G. M. Bennett [28] points out that orientation of the surface molecules and the possibility (if more than one molecular species be present) of a difference between the composition of the surface layer and that of the liquid in bulk, preclude the possibility of surface energy data giving trustworthy information relative to the molecular condition of liquids.

Mechanism of Reactions.

Gaseous reactions which follow the course prescribed by the unimolecular equation have in most cases been proved conclusively to be heterogeneous or surface reactions, and the number for which it is possible to point to substantial evidence in support of the view that they are homogeneous or volume reactions is very limited. Such evidence, although far from conclusive, has been provided in the case of the thermal decomposition of nitrogen pentoxide,[29] the isomeric transformation of *cyclo*propane,[30] and the decomposition of phosphine [31] at sufficiently high temperatures. Further investigation [32] has shown, however, that the first of these reactions is catalysed by the nitrogen peroxide formed, and this fact is sufficient to render extremely doubtful the interpretation which was originally given to the experimental data.

More recently, the thermal decomposition of phosphine has been re-examined [33] with results which seem to justify the conclusion that this is entirely a surface reaction, analogous to the classical case of the decomposition of arsine. The earlier experiments afforded evidence of a change in the value of the temperature coefficient at about 950°, suggesting that the reaction, which is undoubtedly heterogeneous at lower temperatures, is gradually replaced by a homogeneous reaction which predominates at higher temperatures.

[27] R. Schenck and M. Kintzinger, *Rec. trav. chim.*, 1923, **42**, 759; A., 1923, ii, 614.

[28] *J.*, 1924, **125**, 958.

[29] F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53; *A.*, 1921, ii, 249.

[30] M. Trautz and K. Winkler, *J. pr. Chem.*, 1922, [ii], **104**, 53; *A.*, 1922, i, 926.

[31] M. Trautz and D. S. Bhandarkar, *Z. anorg. Chem.*, 1919, **106**, 95; *A.*, 1919, ii, 277.

[32] F. Daniels, O. R. Wulf, and S. Karrer, *J. Amer. Chem. Soc.*, 1922, **44**, 2402; *A.*, 1923, ii, 24; compare also R. H. Lueck, *ibid.*, 1922, **44**, 757; *A.*, 1922, ii, 433.

[33] C. N. Hinshelwood and B. Topley, *J.*, 1924, **125**, 393.

The new experiments show no such alteration in the value of the temperature coefficient, and it follows that the decomposition of phosphine can no longer be accepted as a concrete example of that type of change—the homogeneous unimolecular gas reaction—which has formed the subject of much discussion in recent years.

In the absence of proof of the reality of homogeneous unimolecular chemical reactions, it is not unreasonable to assume that isolated molecules are incapable of chemical change and, in the absence of effects due to the absorption of radiant energy, that such change is to be attributed to collisions between molecules. On kinetic grounds, it may further be expected that the vast majority of reactions which take place in a single stage will be of the bimolecular type.

The experimental data obtained in a recent investigation of the thermal decomposition of nitrous oxide and of chlorine monoxide indicate that both these reactions are bimolecular. Apart from a slight disturbance which appears to be due to the catalysing effect of traces of by-products, the decomposition of nitrous oxide [34] follows a normal course. In the case of chlorine monoxide, there is clear evidence that decomposition occurs in two stages.[35] Both stages, however, are bimolecular and the respective velocity coefficients are of the same order of magnitude, a circumstance which justifies the treatment of the experimental data as if a single stage were involved.

On the assumption that nitrous oxide and chlorine monoxide are decomposed as the result of bimolecular collisions, which are effective when the joint energy of the colliding molecules exceeds a certain critical value, an adequate explanation of the observed facts may be obtained. The critical increment or energy of activation, Q, may be calculated from the temperature coefficient of the reaction velocity. Assuming that every such collision results in the formation of the products of the reaction, it is also possible to derive the value of the critical increment from the measured rate of reaction, in that the velocity is given by

$$v = 2\sqrt{2}\pi n^2\sigma^2\bar{u}e^{-Q/RT},$$

where n is the number of molecules per c.c., $e^{-Q/RT}$ the fraction of the molecules which are activated, σ the molecular diameter, and $\bar{u}$ the root mean square velocity of the molecules. The comparison of the two values of Q was first made by W. C. McC. Lewis,[36]

[34] C. N. Hinshelwood and R. E. Burk, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 284; A., ii, 751.

[35] C. N. Hinshelwood and C. R. Prichard, *J.*, 1923, **123**, 2730.

[36] *J.*, 1918, **113**, 471.

who made use of data relating to the decomposition of hydrogen iodide. The following table [37] includes the results for nitrous oxide, chlorine monoxide, and hydrogen iodide. The heats of activation recorded under Q_1 are those derived from the temperature coefficients of the reactions, those under Q_2 being the values calculated from the measured rate of reaction :

Thermal decomposition of	Q_1.	Q_2.	T.
Nitrous oxide	55,000	58,500	956°
Hydrogen iodide	43,900	44,000	760
Chlorine monoxide	22,000	21,000	384

The agreement between the values Q_1 and Q_2 affords very substantial support for the view that these reactions can be interpreted quite satisfactorily in terms of the collision theory, without assuming the intervention of any such mode of molecular activation as is implied in the radiation theories of chemical change.

The fact that the heats of activation for the three reactions run parallel with the temperatures at which the respective velocity coefficients have the same value (0·0914 gram-mol. per litre per second) would seem to dispose effectively of the objection that the agreement may be accidental.

Other interesting investigations on reaction mechanism, which bear directly on the question of activation by collision and by radiation, have been carried out by R. G. W. Norrish and E. K. Rideal. The experimental data refer to the combination of sulphur with hydrogen and with oxygen at different temperatures, and the results serve to emphasise the importance of an accurate knowledge of temperature coefficients in the elucidation of the mechanism of chemical change. A brief reference to the main facts is desirable.

At temperatures below the boiling point of sulphur, the reaction with hydrogen [38] involves two concurrent changes, one of which takes place in the vapour phase, the other at the surface of the liquid. The velocity of the gaseous reaction is proportional to the pressure of the hydrogen, whilst the speed of the surface reaction [39] is independent of the pressure. The temperature coefficients are respectively 2·19 and 1·48, corresponding with heats of activation represented by 52,400 and 26,200 calories per gram-atom of sulphur at 300°. The first of these critical increments is, within the limits

[37] C. N. Hinshelwood and J. Hughes, *J.*, 1924, **125**, 1841.

[38] R. G. W. Norrish and E. K. Rideal, *J.*, 1923, **123**, 696.

[39] *Idem, ibid.*, p. 1689. The surface reaction is supposed to take place in two stages; in the first, a molecule of hydrogen is adsorbed by the liquid surface, whilst in the second a molecule of hydrogen sulphide is removed.

of error, the same as that for the dissociation of diatomic sulphur molecules.[40]

The gaseous reaction between sulphur and hydrogen is, moreover, catalysed by ultra-violet light [41] and, on the assumption that the active wave-length is that which corresponds with the position of maximum absorption in the ultra-violet spectrum of sulphur vapour ($\lambda = 2750$ Å.), the radiation theory gives 51,670 calories for the critical increment.

At higher temperatures, the combination of sulphur with oxygen is disturbed by the formation of small quantities of sulphur trioxide, but it proceeds normally at lower temperatures (235—305°), and, in agreement with the observations of H. Bodenstein and W. Karo,[42] is found to be almost exclusively a surface reaction. Measurements [43] of the velocity of reaction at different oxygen pressures suggest, however, that the formation of sulphur dioxide is the result of two concurrent and independent surface reactions—in which two different kinds of sulphur molecules are involved—and for these the temperature coefficients yield 25,750 and 37,450 calories, respectively, as the values of the heats of activation at 300°.

On comparing the heats of activation for the six reactions which have been referred to above, it is seen that they all represent simple multiples of a constant quantity, *viz.*, 12,700 calories. This quantity is supposed to represent the amount of energy which is necessary for the activation of a molecule of sulphur and corresponds with the rupture of a valency bond.

The simple relation between the photochemical quantum and the activation energies of the dark reactions leads to the important conclusion that activation of sulphur molecules may be brought about both by collision and by radiation. It seems probable that activation by radiation must be the prelude to a change in which the activated molecules are transformed by collision with other molecules, for, in face of known facts, the deactivation process, whether resulting in the production of molecules of the resultant or in the reformation of molecules of the reactant, cannot be assumed to be unimolecular.

The relations now established in regard to chemical activation seem very difficult to interpret unless it is assumed that activation by collision is a process which, like activation by absorption of radiant energy, is subject to the laws of quantum dynamics.

[40] H. Budde, *Z. anorg. Chem.*, 1912, **58**, 169; *A.*, 1912, ii, 1145.
[41] R. G. W. Norrish and E. K. Rideal, *J.*, 1924, **125**, 2070.
[42] *Z. physikal. Chem.*, 1909, **75**, 30; *A.*, 1910, ii, 1051.
[43] R. G. W. Norrish and E. K. Rideal, *J.*, 1923, **123**, 3202.

Mutarotation of Sugars.

The process of mutarotation in the sugars, where water is supposed to act as a catalyst by forming unstable intermediate compounds with the reactants, has been examined recently [44] by reference to dynamical criteria. That water is added and subsequently removed in these reactions has been the generally accepted view, whether the nature of the intermediate compound is that postulated by E. F. Armstrong [45] or by T. M. Lowry.[46]

Experiments with different sugars and widely varied quantities of water have shown that the mutarotation–time curves are, within the limits of experimental error, exponential as required by the equation $k = 1/t \,.\, \log_e \xi/\xi - x$, where x is the concentration of the β-sugar formed after time t, and ξ is the equilibrium value of x. A rigid mathematical analysis of the dynamics of mutarotation shows, however, that although the x–t curves cannot, on the hydrate theory, be exponential, yet under certain conditions they may approximate very closely to the exponential form.

Assuming that the reaction may be formulated

$$H_2O + S_\alpha \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M \underset{k_4}{\overset{k_3}{\rightleftharpoons}} S_\beta + H_2O,$$

these conditions are that k_1 and k_4 must be small in comparison with k_2 and k_3. When these conditions are fulfilled, it is found, however, that k (the experimental velocity coefficient derived from the rotation data) should be proportional to the amount of water present, in that

$$k = \frac{1}{t} \log_e \xi/\xi - x = b \,.\, \frac{k_1 k_3 + k_2 k_4}{k_2 + k_3},$$

where b is the molar concentration of the water.

Experiments with tetra-acetyl-*d*-glucose in dry and moist ethyl acetate (0·025—0·1% of water) show, however, that the velocity coefficient, k, is independent of the water concentration. In a similar way, experiments with α-glucose in methyl-alcoholic solutions containing up to 2% of water show a wide divergence from the proportionality between the initial velocity and the water concentration which is required by the hydrate theory. On dynamical grounds, it is inferred that mutarotation is essentially a tautomeric reaction in which there is no intervention of water. This was the view put forward by Jacobson and Stelzner,[47] and in support of its

[44] J. W. Baker, C. K. Ingold, and J. F. Thorpe, *J.*, 1924, **125**, 268.
[45] *J.*, 1903, **83**, 1309.
[46] *Ibid.*, p. 1316.
[47] Meyer and Jacobson's "Organische Chemie," 2nd edition, i, (2), 915.

correctness there is corroborative evidence based on the structure of sugars which show mutarotation as compared with those which do not. A similar structural argument against the hydrate theory of mutarotation was advanced some years ago by R. Gilmour.[48]

The mutarotation of beryllium benzoylcamphor examined by H. Burgess and T. M. Lowry [49] is supposed to be analogous to that of α-glucose, and is of particular interest by reason of the fact that in this derivative of benzoylcamphor all the mobile hydrogen has been replaced by a metal.

Measurements of the velocity of inversion of sucrose by acids have occasionally been found to yield abnormally high values for the velocity coefficient in the early stages of the reaction. Although these have been generally attributed to errors of experiment, it would now seem to have been established by S. W. Pennycuick [50] that they correspond with the normal course of the reaction, the velocity, as determined by the polarisation method, being measurably affected in the initial period by the mutarotation of the glucose and fructose formed.

The mutarotational lag due to the glucose can be calculated from the data recorded by C. S. Hudson [51] and by J. M. Nelson and F. M. Beegle; [52] that due to the fructose is less in magnitude, but cannot be evaluated. So far as the mutarotation of the glucose only is concerned, the inversion process may be formulated

$$\text{sucrose} \xrightarrow{k_1} \alpha\text{-glucose} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \beta\text{-glucose},$$

in which $k_2/k_3 = 1{\cdot}67$ is independent of the temperature and the concentration. The magnitude of the lag depends on the ratio $k_1/k_2 + k_3$, which varies with the concentration of the acid catalyst. Under fixed conditions, the lag increases to a maximum value as the reaction proceeds, but after a brief period becomes proportional to the concentration of the residual sucrose.

Polarimetric measurements of the rate of inversion with and without lag are in accord with the theoretical anticipations. In view of the very frequent and varied applications of the acid-catalysed inversion of sucrose, it is interesting to record that the use of the short interval formula $k = 1/(t_2 - t_1) \cdot \log(\lambda_{t_1} - \lambda_\infty)/(\lambda_{t_2} - \lambda_\infty)$ is not interfered with by the mutarotational lag, provided that the initial stage of the reaction is avoided. The graphs obtained by plotting the values of $\log(\lambda_t - \lambda_\infty)$ with and without lag against t

[48] *P.*, 1909, **25**, 225; compare *J.*, 1924, **125**, 705.
[49] *J.*, 1924, **125**, 2081.
[50] *Ibid.*, p. 2049.
[51] *Z. physikal. Chem.*, 1903, **44**, 487; *A.*, 1903, ii, 623.
[52] *J. Amer. Chem. Soc.*, 1919, **41**, 559; *A.*, 1919, i, 256.

consist, for the later stages of the reaction, of accurately parallel straight lines. Incidentally, the results of this inquiry afford an interpretation of the anomalies recorded by M. A. Rosanoff, R. H. Clark, and R. L. Sibley,[53] and show that the suggested analogy [54] between acid catalysis and enzyme action is devoid of foundation.

Periodicity in Chemical Reactions.

Examples of periodicity in the velocity of chemical change have been recorded from time to time, but such periodicity has usually been regarded as an exceptional phenomenon peculiar to certain reacting systems. Recent observations by E. S. Hedges and J. E. Myers [55] indicate, however, that periodic chemical reactions are of very general occurrence. Using a self-registering apparatus of the type known as Ostwald's chemograph, they have investigated the rate of dissolution of metals in acids, alkalis, and other reagents, and have obtained periodic curves similar to those described by Ostwald [56] for the dissolution of a particular (non-reproducible) sample of chromium in hydrochloric acid. Although the automatic records suggest a gradual increase and decrease in the rate at which hydrogen is evolved, this is due to the unavoidable lag of the recording apparatus, for direct manometric readings taken at short intervals of time indicate that the rise of pressure is very rapid. The periodicity consists in variations in the rate of evolution of gas, and not in an alternation of periods in which the metals are successively active and passive. Supersaturation of the solution or of the metal with gas plays no part in the phenomenon. Although the frequency of the periods is a function of the concentration of the reagent, other undetermined factors are operative. The pulses appear to be superimposed on the normal velocity–time curve, and their peaks correspond with a nearly constant value. The presence of a third substance, if only in minute quantity, seems to be essential for the development of periodicity. In particular, it has been found that many metals, after being heated in a vacuum or after other kinds of treatment, acquire the faculty of imparting a periodic character to the rate at which magnesium, aluminium, etc., are dissolved by acids, and it is suggested that such treatment gives rise to metastable forms, which are responsible for the periodicity. The ageing which such activated metals exhibit is supposed to correspond with the gradual return to the stable condition. The

[53] *J. Amer. Chem. Soc.*, 1911, **33**, 1911; *A.*, 1912, ii, 34.

[54] E. F. Armstrong and R. J. Caldwell, *Proc. Roy. Soc.*, 1904, **74**, 195; *A.*, 1904, i, 1070.

[55] *J.*, 1924, **125**, 604.

[56] *Z. physikal. Chem.*, 1900, **35**, 33, 204; *A.*, 1900, ii, 730; 1901, ii, 24.

source of the periodicity is in the second metallic component, and the phenomenon is independent of the dissolution process, for activated platinum causes a periodic evolution of hydrogen from a solution of chromous chloride.

In addition, mercury in its normal condition shows marked activity, its behaviour being very similar to that observed by Bredig [57] in the catalytic decomposition of hydrogen peroxide by this metal. The supposition that other metals, when activated by treatment, would show a periodic catalysing influence on hydrogen peroxide has been fully confirmed [58] by experiment. The phenomenon is consequently of a very general character.

Incidentally, the experiments with mercury and hydrogen peroxide afford substantial grounds for the view that the periodicity of this reaction cannot be due to the alternating formation and disappearance of an oxide film. Film formation often takes place in the absence of periodicity, and, on the other hand, although much more rarely, periodicity is met with in the absence of any visible surface film.

For the time being, these most interesting observations remain unexplained.[59]

Electrode Potentials.

In view of the difficulties which are encountered in the interpretation of the quantity P in the Nernst formula $E = RT/nF \cdot \log P/p$ for electrode potential difference, it is generally conceded that this formula cannot be regarded as more than a purely formal method of depicting the relations which characterise a reversible electrode. The difficulties in question are, of course, very largely exaggerated by the assumption that electrolytic solution pressures, whatever their magnitude, conform to the requirements of the simple gas laws. The assumption that the ions collectively are incompressible would very probably be much nearer the truth, and this leads to the formula $E = (P - p)v/nF$,[60] in which v is the ionic volume. For a given electrode potential, this formula yields very much smaller values for the electrolytic solution

[57] G. Bredig and I. Weinmayr, *Z. physikal. Chem.*, 1903, **42**, 601; *A.*, 1903, ii, 279.

[58] E. S. Hedges and J. E. Myers, *J.*, 1924, **125**, 1282.

[59] According to a private communication from Dr. Myers, the difference of potential between a periodically dissolving metal and the acid solvent shows periodic variations which synchronise with the periodicity in the rate of gas evolution. Further, it has been observed that there is a difference of potential between the activated and inactive forms of a metal when these are immersed in an acid solution.

[60] A. W. Porter, *Trans. Faraday Soc.*, 1924, **19**, 817.

pressure, P, than are given by the logarithmic equation. Similar attempts to provide a physical basis for the Nernst formula have not, however, been regarded with favour, and during the last few years the possible existence of a true Volta contact effect, measurable in terms of the electron affinities of the metals, has been seriously considered [61] as an alternative to the hypothetical electrolytic solution pressure presumed by Nernst.

The electron affinity, ϕ, which is a characteristic and fundamental quantity, may be calculated from Richardson's thermionic equation, which expresses the influence of temperature on the thermionic electron emission. It has already been shown that photo-electric effects and contact potential differences [62] in high vacua can be interpreted in terms of this characteristic quantity. If the values of ϕ for different metals are arranged in order of magnitude, a series is obtained which is very much the same as the ordinary electrochemical series, but the fact that the *E.M.F.*'s of galvanic combinations are dependent on the concentrations of the electrolytes concerned rules out the possibility of interpreting electrode potentials solely by reference to a quantity which might otherwise be adequate to account for Volta effects. On the assumption that the electromotive behaviour of the metals is mainly determined by their electron affinities, E. K. Rideal [63] has derived a thermodynamic formula for the *E.M.F.* of a cell of the Daniell type which reduces to the accepted form when applied to cells of the concentration and amalgam group. It leads to the conclusion that the difference between the normal electrode potential and the electron affinity of a metal is dependent on the atomic volume of the latter. In so far as the relation can be tested, it appears to receive some support from the available data. Whilst the argument underlying this equation is intended to show the untenability of Nernst's conception of electrolytic solution pressure, it is claimed by J. A. V. Butler [64] that an adequate and physically acceptable basis for the Nernst formula is to hand when the conditions at the boundary surface of a reversible electrode are subjected to statistical analysis. The considerations advanced are similar to those used by Langmuir in the theoretical treatment of the kinetics of vaporisation and of heterogeneous gas reactions, and an equation is obtained in which the normal electrode potential is represented as the sum of the heat absorbed in the passage of the metal ions into solution and of a quantity which is determined by the statistical conditions at the surface of the electrode.

[61] I. Langmuir, *Trans. Amer. Electrochem. Soc.*, 1916, **29**, 125.
[62] R. A. Millikan, *Physical Rev.*, 1921, **18**, 236.
[63] *Trans. Faraday Soc.*, 1924, **19**, 667.
[64] *Ibid.*, 729; *A.*, ii, 598.

In view of the fundamental difference of attitude towards the Nernst conception, it is of interest to note that the equations derived by the above authors for the normal potential are of the same type, *viz.*, $E_0 = A + RT/nF.\log f(M)$. In the one case, A represents the electron affinity and $f(M)$ the atomic volume of the metal, whilst in the other, A is the heat of solution of the ions and $f(M)$ is a quantity which depends on the number of metal ions per square centimetre of the metal surface and for which a simple kinetic interpretation is suggested.

The theory of allotropic equilibrium has been advanced by Smits [65] in explanation of the electromotive behaviour of the metals, and other attempts to elucidate the factors which determine the normal electrode potential have been made by D. Reichinstein,[66] J. Heyrovský,[67] and R. D. Kleeman.[68] The last-named suggests that the potential difference is due to the formation of a transition layer in which the ions are segregated by reason of the difference in the velocities of diffusion of the positive and negative ions, and that the tendency of the metal to pass into solution is of secondary importance.

A convenient substitute for the ordinary hydrogen electrode is the quinhydrone electrode described originally by E. Biilmann.[69] It represents a hydrogen electrode of very low pressure, the value of this being determined by the concentration of the hydrogen which is in equilibrium with the quinone and hydroquinone which are formed when quinhydrone is dissolved in water. Application of the mass law to the system $C_6H_4O_2 + H_2 \rightleftarrows C_6H_4(OH)_2$ shows that this concentration is determined at a given temperature by the ratio of the concentrations of the hydroquinone and quinone.

The advantages of this electrode are that it can be quickly set up, affords a constant difference of potential very soon after the platinum wire or foil has been placed in the solution, and may be used when the ordinary hydrogen electrode is inadmissible because of the reducing action of hydrogen (at atmospheric pressure) on substances present in the electrode solution. On the other hand, hydroquinone is a weak acid (ionisation constant $= 1{\cdot}1 \times 10^{-10}$) and this imposes limitations on the use of the quinhydrone electrode with solutions of basic substances, whilst the oxidising properties of quinone may be the cause of disturbance in solutions which contain readily oxidisable substances.

[65] "Theory of Allotropy," transl. J. S. Thomas, Chapter VII.
[66] *Z. physikal. Chem.*, 1920, **95**, 472; *A.*, 1920, ii, 729.
[67] *Proc. Roy. Soc.*, 1923, [*A*], **102**, 638; *A.*, 1923, ii, 114.
[68] *Physical Rev.*, 1922, **20**, 174.
[69] *Ann. Chim.*, 1921, [ix], **15**, 109; *A.*, 1921, ii, 372; E. Biilmann and H. Lund, *ibid.*, 1921, [ix], **16**, 321; *A.*, 1922, ii, 111.

With 0·01*N*-HCl + 0·09*N*-KCl as the electrolyte, the quinhydrone electrode has been found to give an accurately reproducible potential difference of 0·7040 ± 0·0002 [70] volt when measured against a hydrogen electrode in the same electrolyte. In the matter of reproducibility, it is quite as good as the 3·5*N*-calomel electrode and distinctly better than the 0·1*N*-calomel electrode, with which good results are not obtained unless the calomel is fractionated by washing with the production of a fine-grained sample.

The general utility of the quinhydrone electrode has been demonstrated by various experimenters who have used it in titrimetric work,[71] in the estimation of amino-acids,[72] in the study of the ionisation of dibasic acids [73] and transition acids,[74] and, further, in the determination of the reduction potentials of various types of organic compounds such as the quinones [75] and azo-compounds.[76] It has also been applied to acetone–water mixtures [77] with results which indicate that definite potential values are obtained just as readily as in pure water. For a series of organic bases examined in water and acetone–water mixtures containing 50 and 90% of acetone, it is found that the ionisation constants fall very rapidly with increase in the acetone content of the solvent, but there is, in general, no change in the order of the bases when these are arranged according to the magnitude of the ionisation constants. None of the formulæ previously suggested for the connexion between the ionisation constants and the dielectric capacities of the solvents is in agreement with the data obtained in this investigation.

Irreversible Electrode Phenomena.

In contradistinction to the reversible electrode processes with which thermodynamic formulæ are concerned, all actual processes are to a greater or less extent irreversible. For a particular process taking place under specified conditions, the departure of the actual electrode potential difference from the corresponding equilibrium value affords a measure of the degree of irreversibility of the electrode reaction under these conditions. A very clear and valuable summary of the present state of our knowledge of such irreversible

[70] S. Veibel, *J.*, 1923, **123**, 2203.
[71] I. M. Kolthoff, *Rec. trav. chim.*, 1923, **42**, 186; *A.*, 1923, ii, 247.
[72] L. J. Harris, *J.*, 1923, **123**, 3294.
[73] E. L. Larsson, *Z. anorg. Chem.*, 1922, **125**, 287; *A.*, 1923, ii, 55.
[74] E. Schreiner, *Z. physikal. Chem.*, 1922, **122**, 201; *A.*, 1922, ii, 736.
[75] J. B. Conant, H. M. Kahn, L. F. Fieser, and S. S. Kurtz, *J. Amer. Chem. Soc.*, 1922, **44**, 1382; *A.*, 1922, ii, 547; J. B. Conant and L. F. Fieser, *ibid.*, 1923, **45**, 2194.
[76] E. Biilmann, *Trans. Faraday Soc.*, 1924, **19**, 676.
[77] J. N. Pring, *ibid.*, p. 705.

electrode processes has been compiled by H. J. T. Ellingham and A. J. Allmand as an introduction to a Faraday Society discussion of the subject.[78] In this the authors emphasise the fact that the majority of polarisation effects are probably due to the finite and relatively small velocity of those compensating processes (diffusion, chemical reaction, etc.) which counteract the effect of the primary electrode reaction. That the polarisation in some cases must be, at least in part, ascribed to the formation of a gas film on the electrode surface would seem, however, to be rendered necessary by the evidence [79] which has been advanced in support of this alternative mechanism.

In electrode reactions which are accompanied by gas evolution, the term overvoltage [80] is generally used to designate the difference between the reversible potential of the gas electrode and the potential which comes into play when the gas in question is being liberated from the same solution by the passage of a current of specified density. In the attempt to measure overvoltage, as thus defined, two methods have been employed. By the direct method, the polarisation is measured with the polarising current in action, but in the commutator method, the polarising current is periodically interrupted by a suitable device, and the electrode potential measured during the interruption of the primary current. Results yielded by this method depend on the speed of commutation, but it is claimed that accurate and reproducible values are obtained when the rate of interruption is sufficiently rapid and the current density exceeds a certain critical value.

Under conditions which afford reproducible values of polarisation there is wide divergence between the values given by the direct and commutator methods and it is fairly obvious that the quantities measured are not the same. The smaller values given by the commutator method are considered by E. Newbery,[81] J. N. Pring,[82] H. J. S. Sand and E. J. Weeks [83] to be a correct measure of overvoltage, the higher values obtained by the direct method being attributed to the existence of an ohmic resistance (the so-called "transfer resistance" which opposes the penetration of the ions into the electrode surface), which is included in the directly measured polarisation.

[78] J. N. Pring, *Trans. Faraday Soc.*, 1924, **19**, 748.

[79] N. V. S. Knibbs, *ibid.*, p. 800.

[80] The present conventional significance differs somewhat from that given originally to the term overvoltage by Caspari (*Z. physikal. Chem.*, 1899, **30**, 89).

[81] *J.*, 1914, **105**, 2419; 1916, **109**, 1051, 1066, 1107, 1359; 1924, **125**, 511

[82] *Z. Elektrochem.*, 1913, **19**, 255; *A.*, 1913, ii, 380.

[83] *J.*, 1923, **123**, 2896; compare also Sand, Weeks, and Worrell, *ibid.*, p. 456.

On the other hand, many workers have questioned the reality of "transfer resistance," and in ascribing the divergence of the results to errors inherent in the commutator method have contended that the latter does not afford a means of measuring overvoltage in the accepted sense of this term. The experiments carried out by D. A. MacInnes,[84] S. Dunnill,[85] H. V. Tartar and H. E. Keyes,[86] A. L. Ferguson and G. van Zyl,[87] and by S. Glasstone [88] afford, directly or indirectly, evidence for this view. The observations in question have reference to the overvoltage of hydrogen, and it would seem to have been established that the difference is in part due to the very rapid fall in potential which occurs when the polarising current is interrupted. A further consideration is that the maximum concentration of hydrogen in the electrode surface layer will of necessity be less when the current is intermittent than when it is continuous, for in the former case greater opportunity is afforded for the removal of the hydrogen by the compensating processes. The suggestion has also been made that induced alternating currents will have a similar effect in reducing the measured overvoltage below the true value. Further evidence for the non-existence of transfer resistance effects would seem to be afforded by the oscillographic records obtained by R. T. Lattey [89] and by the observations of J. Heyrovský [90] on the overvoltage at a dropping mercury electrode, at which, it may be noted, there is no indication of the formation of any kind of surface film. Finally, by measuring the rate of fall of potential of a polarised hydrogen electrode and extrapolating the potential difference–time curve to zero time, values [91] have been obtained for small polarising currents which are very nearly the same as those given by the direct method. This result is difficult to reconcile with the transfer resistance hypothesis, but, on the other hand, it must be kept in mind that the equality is confined to a limited range of current densities. In general, the inequality is such that no simple hypothesis would seem to account for the facts. Experiments, described by Newbery,[92] in which a comparison has been made between the polarisation potentials measured by the

[84] D. A. MacInnes and L. Adler, *J. Amer. Chem. Soc.*, 1919, **41**, 194; *A.*, 1919, ii, 131; D. A. MacInnes and A. W. Contieri, *ibid.*, p. 2013; *A.*, 1919, ii, 77.

[85] *J.*, 1921, **119**, 1081.

[86] *J. Amer. Chem. Soc.*, 1922, **44** 557; *A.*, 1922, ii, 343.

[87] *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 337; *A.*, ii, 458.

[88] *J.*, 1923, **123**, 1745, 2936.

[89] *Trans. Faraday Soc.*, 1924, **19**, 829.

[90] *Ibid.*, p. 785; *A.*, ii, 509.

[91] S. Glasstone, *J.*, 1924, **125**, 250.

[92] *Ibid.*, p. 511.

direct and commutator methods show that the directly measured values always increase with the current density, whereas the commutator values show a decrease when certain electrodes are used. Facts of this kind warrant the belief that the interpretation of irreversible electrode phenomena may require the acceptance of some such hypothesis as that postulated by Newbery,[93] according to which polarisation effects are largely determined by the stability of unstable overvoltage compounds formed by combination of the hydrogen with the metal of the electrode.

The dependence of the cathodic overvoltage, E, on the current density, I, is usually represented by the logarithmic formula $E = a + b \log I$, in which a and b are constants. This equation, originally put forward by J. Tafel,[94] has been derived from other theoretical considerations by G. M. Westrip[95] and expresses fairly well the results obtained by this author for zinc, copper, and brass cathodes. The formula assumes that the current is proportional to the rate at which atomic hydrogen is removed in the form of molecules, and no allowance is made for the dispersal by diffusion into the electrode and electrolyte. Taking this into account, the formula becomes $E = a + b \log (I - c)$,[96] in which c is a third constant. Whilst, on the one hand, the overvoltage data for a lead cathode are in excellent agreement with this equation, it is found that the behaviour of a mercury cathode can be expressed by the simpler formula. Since, moreover, the simpler relation holds for very low current densities, it appears that very little hydrogen is removed from the mercury surface by diffusion. This is consistent with the fact that the maximum current which can pass without visible evolution of gas ("residual current") is very much smaller with a mercury cathode than it is for a cathode of lead.

The minimum overvoltage, corresponding with the commencement of visible gas formation, should, according to theory, be independent of the nature of the electrolyte, and experiments made by Glasstone[97] with a lead cathode show that there is very little change when the hydrion concentration is varied from 1 to $1 \cdot 10^{-11}$ gram-ion per litre. On the other hand, results obtained[98] with alkaline solutions and an antimony cathode are said to indicate that the overvoltage, measured by the commutator method with current densities sufficiently large to give reproducible results, is a linear function of the "p_H voltage"—a term applied to the difference of potential between the saturated calomel electrode and a hydrogen

[93] *J.*, 1916, **109**, 1107; compare *Ann. Reports*, 1917, 14.
[94] *Z. physikal. Chem.*, 1905, **50**, 641; *A.*, 1905, ii, 223.
[95] *J.*, 1924, **125**, 1112. [96] S. Glasstone, *J.*, 1924, **125**, 2414.
[97] *Loc. cit.* [98] H. J. S. Sand and E. J. Weeks, *J.*, 1924, **125**, 160.

electrode immersed in the electrolyte in question. These results are not necessarily contradictory, for the hydrion concentrations of the solutions examined do not overlap.

Trustworthy measurements of the influence of pressure on overvoltage are not available, but concordant data [99] show that the overvoltage at a mercury cathode decreases with rise of temperature by about 2 millivolts per degree. The temperature coefficient at low current densities appears to be much greater for cathodes with a low overvoltage value than for those which have a high overvoltage.[1] At low current densities, the influence of temperature is mainly determined by the temperature coefficient of the compensating processes, whereas at high current densities, when the electrode is covered by a gas film, the dominant factor is the influence of temperature on the ease with which bubbles of gas are liberated. Overvoltages and their temperature coefficients thus tend to become independent of the nature of the cathode at high current densities.[2]

Experiments with binary alloy cathodes [3] show that the overvoltage is independent of the proportions of the metals in the alloy and is determined by that component which in the pure state has the smaller overvoltage.

Electrolytes.

The progress of inquiry into the nature of electrolytes and the properties of their solutions appears to have reached a stage where the whole system of ionic chemistry, in the form given to it by the theory of Arrhenius, is seriously threatened. This theory has been almost universally adopted as the simplest and most convenient medium for the discussion of all kinds of problems connected with solutions of electrolytes, although it has been recognised that it fails to provide more than a purely qualitative interpretation of many known facts and that such facts may not infrequently be explained in other ways. The considerations advanced by S. R. Milner [4] in support of the view that the osmotic and electrical properties of salt solutions can be interpreted without assuming variations in the degree of ionisation have probably not received the attention to which they are entitled. So far as Milner's theory is concerned, this is mainly due to the abstract nature of the mathe-

[99] S. Glasstone, *loc. cit.*; S. J. Bircher and W. D. Harkins, *J. Amer. Chem. Soc.*, 1923, **45**, 2897; A., 1924, ii, 88.

[1] E. K. Rideal, *J. Amer. Chem. Soc.*, 1920, **42**, 94; *A.*, 1920, ii, 364.

[2] M. Knobel, P. Caplan, and M. Eiseman, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 51.

[3] P. Fischer, *Z. physikal. Chem.*, 1924, **113**, 326.

[4] *Phil. Mag.*, 1912, [vi], **23**, 551; 1913, [vi], **25**, 742; *A.*, 1913, ii, 481; *ibid.*, 1918, [vi], **35**, 352.

matical considerations involved and to the circumstance that the consequences of the theory have not been worked out in detail, whilst in the case of the theory put forward by J. C. Ghosh [5] the fundamental postulates have failed to meet with general acceptance.

In the last few years, the discussion of the general problem of solution has been marked by the substitution of the concept of thermodynamic concentration for the familiar volume concentration. It would seem to have been established that the discrepancies between the results of experiment on the one hand, and thermodynamic theory on the other, are for the most part to be attributed to the erroneous assumption that the activities of the components of a solution are to be measured by their respective molar concentrations. Such discrepancies cover a very wide range of properties and phenomena, including, for instance, osmotic properties, electrical conductance, electrode potentials, partition and solubility relations, and the application of the mass law whether to systems in equilibrium or to systems in process of change.

Methods for the determination of the activities of the components of a solution—solute, solvent, molecules, and ions—have been worked out by G. N. Lewis and his collaborators. For a detailed account of these methods reference may be made to that extraordinarily interesting work by Lewis and Randall,[6] in which the authors describe and illustrate many novel applications of thermodynamics to chemical problems. The deviation of actual from ideal behaviour may be conveniently expressed by the activity coefficient (α = ratio of activity to concentration), which may be defined as the factor by which the concentrations must be multiplied in order to make the expressions for mass action and free energy applicable to actual as distinguished from ideal solutes. Alternative and independent methods of evaluation are shown to afford consistent values for the activity coefficient.

The utility of the concept of activity has been fully realised in recent work on solutions of electrolytes. The ionic constituents of such solutions have activity coefficients which, even in dilute solutions, are determined by the electrical forces between the ions. Such forces depend on the magnitude of the ionic charges (valencies), on the average distance between the ions, and on the dielectric capacity of the medium. For an account of the attempts, prior to 1922, to evaluate the influence of these factors, the reader may be referred to a very interesting summary by L. Ebert.[7] Since

[5] *J.*, 1918, **113**, 449, 627, 707, 790.

[6] "Thermodynamics and the Free Energy of Chemical Substances," by G. N. Lewis and M. Randall. McGraw, Hill Book Co., 1923.

[7] *Jahrb. Radioaktiv. Elektronik*, 1921, **18**, 134.

that time there has been a considerable amount of experimental work [8] bearing on the question, but the most noteworthy publication is a theory advanced by P. Debye and E. Hückel,[9] the scope and character of which suggest that a real advance has been made in the treatment of the problem. The essential features of this theory have been re-presented in a simplified and critical form by A. A. Noyes.[10]

Adopting the symbols used by the latter, the difference per mole between the energy of an ion of valency ν in a solution (S) for which the total ion concentration is c moles per c.c., and the energy of the same ion in a solution (S_0) for which the ion concentration (c_0) is infinitesimal, is represented by

$$\Delta U = A\nu^2\sqrt{\Sigma c\nu^2}/K^{3/2}T^{1/2},$$

where A is a universal constant $= e^3N^2\sqrt{\pi/R} = 7{\cdot}77 \times 10^{15}$, $\Sigma c\nu^2$ is the sum of the products of the concentration and the square of the ionic valency, K is the dielectric capacity of the medium, and T the absolute temperature.

This energy difference is shown by Noyes to bear a simple relation to ΔH, the energy change associated with the thermodynamic transfer of one mole ion from an infinite volume of the more concentrated to an infinite volume of the dilute solution. The ratio $\Delta U/\Delta H = 2/3$. From this relation, the decrease of free energy associated with the transfer of one mole ion from S to S_0 is given by

$$-\Delta F = RT \log_e c/c_0 - A\nu^2\sqrt{\Sigma c\nu^2}/K^{3/2}T^{1/2}$$

When this equation is combined with $-\Delta F = RT \log_e c\alpha/c_0$, where α is the activity coefficient of the ion in solution S, we obtain for the logarithm of α

$$\log_e \alpha = -A\nu^2\sqrt{\Sigma c\nu^2}/R(KT)^{3/2},$$

According to this last equation, the activity coefficients of all ions of the same valency should be identical when the molar concentrations are equal. Although the experimental data for

[8] N. Bjerrum, *Z. physikal. Chem.*, 1923, **104**, 406; *A.*, 1923, ii, 467; *Z. anorg. Chem.*, 1923, **129**, 323; *A.*, 1924, ii, 24; *Z. physikal. Chem.*, 1924, **108**, 82; *A.*, ii, 240. E. Schreiner, *Z. anorg. Chem.*, 1922, **121**, 321; *A.*, 1922, ii, 468; *ibid.*, 1922, **112**, 201; *A.*, 1922, ii, 736; *ibid.*, 1924, **135**, 333; *A.*, ii, 524. J. N. Brönsted, *Z. physikal. Chem.*, 1922, **100**, 139; *A.*, 1922, ii, 354; *J. Amer. Chem. Soc.*, 1922, **44**, 877; *A.*, 1922, ii, 481; *ibid.*, 1922, **44**, 938; *A.*, 1922, ii, 482; *Z. physikal. Chem.*, 1922, **102**, 169; *A.*, 1922, ii, 699; J. N. Brönsted and K. Pedersen, *ibid.*, 1922, **103**, 307; *A.*, 1923, ii, 61; J. N. Brönsted, *J. Amer. Chem. Soc.*, 1923, **45**, 2898; *A.*, 1924, ii, 94.

[9] *Physikal. Z.*, 1923, **24**, 185; *A.*, 1923, ii, 459.

[10] *J. Amer. Chem. Soc.*, 1924, **46**, 1080; *A.*, ii, 658.

electrolytes of the same type show that this is not strictly true, there is on the whole a very fair agreement between the predictions of the theory and the results of actual measurement.[11] The deviations are probably due to differences in the ionic dimensions. For electrolytes of different valency types, the variations in the activity indicated by experiment are almost exactly those predicted by the theory.

The theoretical treatment of the problem offered by Debye and Hückel should help to remove the impression that most of the experimental work carried out in connexion with the theory of complete ionisation is concerned with the proof of relations which are essentially empirical in character. It is true that the activity and osmotic coefficients, which are in common use in modern work on solutions, are thermodynamically connected, but the functional dependence of these coefficients on the concentration and on the valency type of the electrolyte has been usually represented by empirical formulæ[12] fitted to the experimental data. These empirical formulæ have now been shown to follow directly from the equations of Debye and Hückel, whose theory may be said to mark a new epoch in the consideration of solutions of electrolytes.

H. M. Dawson.

[11] A. A. Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1098; *A.*, ii, 659.

[12] Compare J. N. Brönsted and V. K. La Mer, *ibid.*, p. 555; *A.*, ii, 306.

INORGANIC CHEMISTRY.

The bulk of experimental work published continues to increase and so much is of interest that it has proved unusually difficult to make a fair and representative selection of papers for mention in this Report. While steady progress is made in applying and testing the electronic theories of valency, papers devoted solely to their discussion are few and do not call for special mention. Further work and controversy on the subject of the reflection of characteristic *X*-rays by the atoms in a crystal, which is likely to become of the greatest importance in determining the detailed structure of inorganic compounds,[1] will be discussed in the Report on Crystallography.

Atomic Weights.

Carbon.—Pure silver cyanide was heated at 270° in pure hydrogen in glass or silica flasks and thus reduced to metallic silver : in another series of determinations pure silver cyanate was similarly reduced. Assuming Ag = 107·88 and N = 14·008, twenty-one determinations of the ratio AgCN : Ag give C = 12·002 ± 0·001 and sixteen determinations of the ratio AgCNO : Ag give C = 12·003 ± 0·001. By combining these ratios, values for cyanogen (CN = 26·008) and silver (Ag = 107·871) may be deduced relative to O=16 without assumption : if this value for cyanogen is accepted and the well-established value N = 14·008 assumed, the atomic weight of carbon is C = 12·000.[2] The value now obtained for silver, identical with that deduced from the ratios $LiClO_4$: LiCl and LiCl : Ag,[3] affords strong evidence that the accepted value Ag = 107·88 is certainly too high by about 0·01%.

Nitrogen.—Redeterminations of the density of pure nitrogen, prepared by the ignition of sodium azide, give the mean value N = 14·008.[4]

Sodium.—Eight determinations by conversion of sodium azide into sodium nitrate give for the ratio $NaNO_3$: NaN_3 values ranging from 1·30731 to 1·30738, whence, assuming N = 14·008, Na = 22·998 ± 0·002.[5] Ten concordant determinations, giving in mean

[1] *Ann. Report*, 1923, **20**, 29, 254.
[2] G. Dean, *J.*, 1924, **125**, 2656.
[3] T. W. Richards and H. H. Willard, *J. Amer. Chem. Soc.*, 1910, **32**, 24.
[4] E. Moles and J. M. Clavera, *J. Chim. Phys.*, 1924, **21**, 10; *A.*, ii, 452.
[5] *Idem*, *Z. physikal. Chem.*, 1923, **107**, 423; *A.*, ii, 174.

the value 1·45422±0·0000077 for the ratio $NaNO_3$: NaCl, considered in conjunction with the values of Richards and Wells for the ratios AgCl : Ag and NaCl : Ag and assuming N = 14·008, give for the atomic weights of sodium, silver, and chlorine the values Na = 22·9985, Ag = 107·88 and Cl = 35·457.[6]

Aluminium.—Aluminium chloride was synthesised from its elements, repeatedly sublimed in pure nitrogen and in a vacuum, distilled into bulbs, weighed, and used for determinations of the ratio $AlCl_3$: 3Ag by the usual method of gravi-volumetric titration. The mean of eleven results ranging from 26·962 to 26·978 is Al = 26·972 ± 0·001.[7]

Chlorine.—Direct gravimetric determination of the weight of silver chloride precipitated by hydrogen chloride from a solution of weighed silver in nitric acid has given for the ratio Ag : AgCl a mean value 100 : 132·863 ± 0·0009,[8] in close agreement with the value of Richards and Wells.[9]

Cobalt.—Samples of cobaltous chloride, prepared from a meteorite of unknown history and from terrestrial sources, were dried and sublimed in hydrogen chloride, fused and weighed in a quartz boat, and analysed by titration with weighed silver in the usual way. Three determinations of the ratio $CoCl_2$: 2Ag for meteoritic material gave the mean value Co = 58·942, seven determinations upon terrestrial cobalt gave in mean the substantially identical result Co = 58·940.[10] The final mean, however, is lower by 0·03 than that found in previous investigations.[11]

Copper.—Pure cupric oxide was heated first at 1000° in air and then at 800° in oxygen and weighed quantities were then reduced in hydrogen at 700—750°. Eight determinations thus of the ratio CuO : Cu gave in mean Cu = 63·546 ± 0·003.[12]

Germanium.—Germanium tetrachloride, prepared from zinc oxide residues and purified by fractional distillation in a vacuum, was used for determinations of the ratio $GeCl_4$: 4Ag, giving in mean Ge = 72·60.[13]

Bromine.—Purified bromine, distilled in an evacuated glass

[6] E. Zintl and A. Meuwsen, *Z. anorg. Chem.*, 1924, **136**, 223; *A.*, ii, 608.

[7] H. Krepelka, *J. Amer. Chem. Soc.*, 1924, **46**, 1343; *A.*, ii, 763.

[8] R. Lorenz and E. Bergheimer, *Z. anorg. Chem.*, 1924, **138**, 205; *A.*, ii, 679.

[9] T. W. Richards and H. L. Wells, *Publ. Carnegie Inst. Wash.*, 1905, No. 28.

[10] G. P. Baxter and M. J. Dorcas, *J. Amer. Chem. Soc.*, 1924, **46**, 357; *A.*, ii, 341.

[11] T. W. Richards and G. P. Baxter, *A.*, 1900, ii, 78; G. P. Baxter and F. B. Coffin, *A.*, 1906, ii, 858.

[12] R. Ruer and K. Bode, *Z. anorg. Chem.*, 1924, **137**, 101; *A.*, ii, 761.

[13] G. P. Baxter and W. C. Cooper, jun., *Proc. Amer. Acad. Arts Sci.*, 1924, **59**, 235; *A.*, ii, 690.

apparatus, was collected in bulbs, weighed, reduced with excess of ammoniacal ammonium arsenite, and titrated nephelometrically with weighed silver : the resulting silver bromide was also collected, dried, and weighed. Ten determinations of the ratio Br : Ag and nine determinations of the ratio Br : AgBr give in mean Br = 79·916 (Ag = 107·880).[14]

Yttrium.—Yttria freed from other earths, especially holmium, by fractional crystallisation as bromate, preceded and followed by fractional precipitation with ammonia, was further purified by precipitation as chloride, by saturating its aqueous solution at 0° with hydrogen chloride, and used for determinations of the ratios $YCl_3 : 3AgCl$ and $YCl_3 : 3Ag$. The results with the purest fraction gave in mean Y = 88·950 ± 0·010, in agreement with Aston's conclusion that yttrium is a simple element of atomic weight 89.[15]

Antimony.—Two important determinations for this element have to be recorded. In one investigation antimonic acid, purified by repeated precipitation as chloroantimonic acid from a solution of antimony pentachloride saturated with hydrogen chloride, was reduced to metal in pure hydrogen. Samples of the trichloride and tribromide prepared from this metal were then fractionally distilled, first in pure nitrogen and then in a vacuum, and used for determinations of the ratios to silver and silver halide, 32 concordant analyses giving in mean Sb = 121·76 (Ag = 107·88; Cl = 35·457; Br = 79·916).[16]

In another case, Kahlbaum's purest antimony was twice fused in hydrogen and combined with pure chlorine, and the antimony trichloride was repeatedly distilled in an evacuated glass apparatus, considerable head and tail fractions being rejected in each distillation. Nine samples collected in weighed bulbs from the main fractions of six of the later distillations, used for determinations of the ratio $SbCl_3 : 3Ag$ in the usual way, gave in mean Sb = 121·748 ± 0·00086,[17] in good agreement with the preceding value and with that of Willard and McAlpine (Sb = 121·77),[18] but much higher than the older value (Sb = 120·2).

One point may well be stressed in connexion with these results. In view of the widely differing atomic weights found by Muzaffar [19]

[14] O. Hönigschmid and E. Zintl, *Annalen*, 1923, **433**, 201; *A.*, ii, 35.
[15] O. Hönigschmid and A. Meuwsen, *Z. anorg. Chem.*, 1924, **140**, 341; *A.*, ii, 860.
[16] O. Hönigschmid, E. Zintl, and M. Linhard, *ibid.*, **136**, 257; *A.*, ii, 619.
[17] P. F. Weatherill, *J. Amer. Chem. Soc.*, 1924, **46**, 2437.
[18] H. H. Willard and R. K. McAlpine, *ibid.*, 1921, **43**, 797; *A.*, 1921, ii, 405.
[19] *Ann. Report*, 1923, **20**, 31.

for antimony from various known sources, it is obviously most unfortunate that both these excellent determinations were made upon samples of antimony of unknown origin. In order that every determination of atomic weight may add its quota to our knowledge of isotopy and of the origin of the elements, it is now essential that the origin of the material investigated shall be ascertained with the greatest possible precision.

Lead.—Lead tetraphenyl, prepared from lead extracted from a Vesuvian cotunnite, was purified by alternate crystallisations from benzene and chloroform and by treatment with absolute alcohol. Weighed quantities were then converted directly to lead bromide by treatment with bromine. Determinations thus of the ratio $Pb(C_6H_5)_4 : PbBr_2$ gave in mean the value Pb = 207·050, appreciably lower than the value (207·192) obtained by the same method for ordinary lead.[20]

The Effect of Intensive Drying.

Important contributions have been made to our knowledge of the effect of intensive drying. Further experiments [21] have confirmed that benzene, even after drying for less than a year, behaves as a mixture and on distillation shows a progressive rise of temperature both in the liquid and in the vapour, the maximum temperature observed being 87·7° in the vapour.[22]

The behaviour of sulphur trioxide has been a mystery ever since Marignac, more than seventy years ago, observed that this substance existed in two solid forms, a mystery which has but been deepened by recent investigations.[23] Smits and Schoenmaker have now [24] discussed the earlier results and communicated observations on intensively dried sulphur trioxide which shed much light on this difficult problem. Pure sulphur trioxide was distilled into an apparatus consisting of two bulbs connected by a U-tube filled with pure phosphoric oxide and was therein distilled back and forth daily for a month until dry. By the use of ingenious means, for a description of which the original paper must be consulted, the dry material was distilled into a second apparatus provided with a glass-spring manometer and a number of receivers into which fractions of the sulphur trioxide could be distilled and sealed off.

[20] A. Piutti and D. Migliacci, *Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 468; *Gazzetta*, 1924, **54**, 605; *A.*, ii, 181, 859.

[21] Compare *Ann. Report*, 1923, **20**, 32.

[22] A. Smits, *J.*, 1924, **125**, 1068.

[23] Compare *Ann. Report*, 1923, **20**, 51; Le Blanc and Rühle, *Ber. Mat. phys. Klass. Sächs. Akad. Wiss.*, 1922, **74**, 106.

[24] A. Smits and P. Schoenmaker, *J.*, 1924, **125**, 2554.

The results are best expressed by a P–T diagram (Fig. 1), where vapour pressure is plotted against temperature.

The original substance gave the data (×) shown on the curve I: after standing 18 hours, molten at 18°, it gave the pressures (⊗) plotted on curve II. These vapour pressure values rise to a maximum, then fall, then rise again. During the fall in vapour pressure, the solid melts, in this case over a *range* of temperature from 13·3°

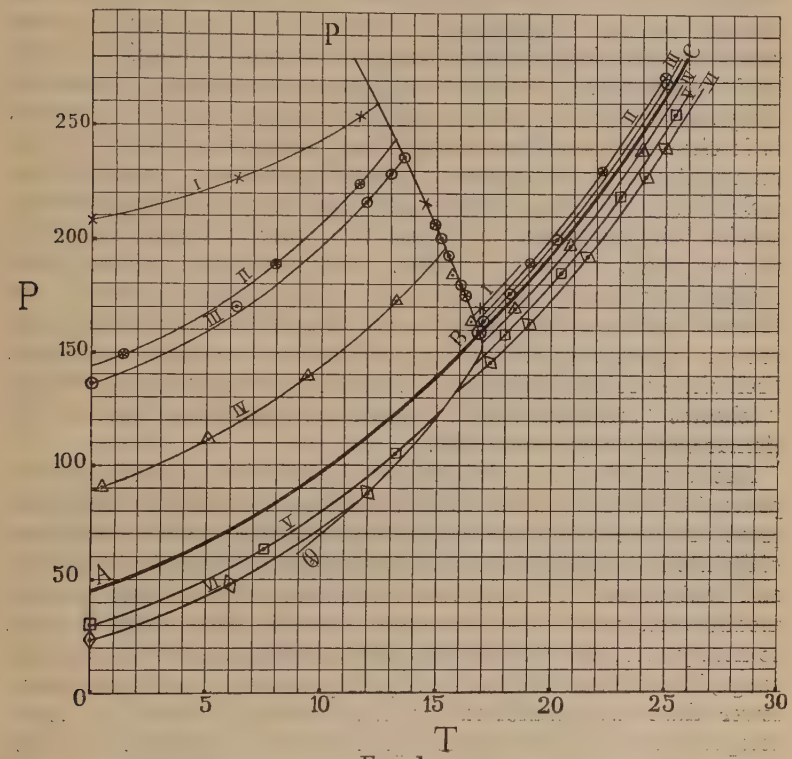


FIG. 1.

to 16·7°. After another 30 hours at 18°, curve III was obtained; and upon evaporating off and removing successive fractions of the sulphur trioxide, the residual material gave successively the curves IV, V and VI.

These curves present the following features: the first portions (on the left), representing in each case the equilibrium between solid and vapour, exhibit a rising vapour pressure but at progressively lower ranges; the middle portions, representing the equilibrium between solid, liquid, and vapour, lie always on the *same* three-phase line PBQ, showing a *fall* of vapour pressure during

melting for fractions above the line ABC and a *rise* of vapour pressure during melting for fractions below that line; the last portions of the curves (to the right of the line PBQ), representing equilibrium between liquid and vapour, show for successive fractions a similar relation to that of the solid–vapour curves but with smaller differences.

It is scarcely necessary to point out that these very remarkable observations are quite unaccountable on the older views of the different states of aggregation: they accord perfectly, however, with the behaviour to be anticipated in the equilibrium solid–liquid–vapour for a system of two components giving a dissociable compound and hence strongly support Smits's theory of allotropy. It is clear that the low-melting "ice" form of sulphur trioxide, with which only the present paper is concerned, contains two molecular species in equilibrium, the transformation between these species being so slowed by intensive drying that the complexity of the system becomes apparent. The varied and puzzling data obtained by previous observers are evidently attributable to the effect of greater or less self-drying of the sulphur trioxide in giving partial evidence of the binary behaviour here fully exhibited. Preliminary results with the "low-melting" and "high-melting" "asbestos" forms of sulphur trioxide show that these, too, exhibit similar complexity when dried.

Another series of experiments[25] showed that pure phosphorus pentoxide (which is, of course, strongly self-drying) exhibited great differences in vapour pressure, according to the conditions of distillation under which it was prepared, and is therefore complex; and that at 400° the metastable sublimate changes into another modification, with a fall in vapour pressure from about 4 atms. to nearly zero, and this transformed solid phase melts over a wide range, beginning at 563° and a vapour pressure (of 0·59 atm.) much lower than that exhibited by the metastable form at lower temperatures. These results again may be explained by, and therefore support, the view that both forms of phosphoric oxide are complex.

In this connexion, it is interesting to note that a detailed examination of the specific heat–temperature curves for a number of liquids shows that some, especially those for benzene, ethylbenzene, and carbon tetrachloride, exhibit irregularities held to indicate that these liquids are associated and undergo molecular changes with change of temperature. These irregularities are much more evident when the liquids have been thoroughly (but not intensively) dried than when they contain a trace of water. Measurements

[25] A. Smits and A. J. Rutgers, *J.*, 1924, **125**, 2573.

of vapour pressure and density over the same range of temperature fail to show any irregularity.[26]

Group I.

Hydrogen is absorbed by cerium and by alloys of cerium with other rare-earth metals above 300°, or, if the metal has previously been melted in a vacuum, rapidly at the ordinary temperature. The products saturated at 20° are greyish-black powders containing nearly 2% by weight of hydrogen, and that prepared from cerium is spontaneously inflammable. When the hydrogen pressure is plotted against the volume of gas absorbed, curves are obtained, similar to those of Hoitsema and Roozeboom for the palladium–hydrogen system, which suggest the formation of two non-miscible solid solutions but afford no evidence that definite hydrides are formed.[27]

Vapour pressure measurements for pure hydrogen-peroxide (99·98% H_2O_2) from 5—90° indicate that the boiling point is 151·1° and the molecular latent heat of evaporation is 11,610 cal.; from the latter value is deduced a value for Trouton's constant, 27·3, showing that liquid hydrogen peroxide is associated. The calculated critical temperature for hydrogen peroxide is 458·8°.[28]

Hydrogen peroxide is stabilised by hydrofluoric acid, but is decomposed by hydrobromic or hydrochloric acid at all concentrations. A detailed investigation for the latter case shows that with low acid concentrations the reaction is unimolecular and oxygen only is evolved, but that for any concentration of hydrogen peroxide there is a critical concentration of hydrochloric acid above which the velocity coefficient becomes proportional to the concentration of acid and both chlorine and oxygen are evolved. It is suggested that the following reactions occur :

(*a*) $H_2O_2 + HCl \rightleftharpoons H_2O_2,HCl$;

(*b*) $H_2O_2,HCl \longrightarrow H_2O{<}^{OH}_{Cl} \longrightarrow H_2O + HOCl$;

(*c*) $HOCl + H_2O_2 \longrightarrow H_2O + O_2 + HCl$;

(*d*) $HOCl + HCl \rightleftharpoons Cl_2 + H_2O$.

The decomposition of hydrogen peroxide by halogens is attributed to the formation of oxy-acids which then react with the peroxide as in (*c*) above.[29]

Despite serious experimental difficulties, it has been shown that in the electrolysis of lithium hydride the hydrogen (at the anode)

[26] J. W. Williams and F. Daniels, *J. Amer. Chem. Soc.*, 1924, **46**, 1569; for details of the apparatus and method, see *ibid.*, p. 903; *A.*, ii, 589, 450.

[27] A. Sieverts and G. Müller-Goldegg, *Z. anorg. Chem.*, 1924, **131**, 65; *A.*, ii, 185.

[28] O. Maas and P. G. Hiebert, *J. Amer. Chem. Soc.*, 1924, **46**, 2693.

[29] *Idem*, *ibid.*, p. 290; *A.*, ii, 326.

and lithium are evolved in the relative amounts required by Faraday's law.[30] This affords further evidence that in the hydrides of the alkali and alkaline-earth metals hydrogen acts as a halogen.[31]

Investigation of the vapour pressures of systems of water with lithium chloride, bromide, and iodide shows that each forms hydrates with 3, 2, and 1 mols. of water, and the iodide a fourth hydrate also with 0·5 mol. of water.[32]

By rapidly heating lithium monosulphide to 360° in a vacuum and treating the product with hydrogen sulphide diluted with hydrogen, nearly pure lithium sulphide is obtained as a buff-coloured powder. Alcoholic solutions of the sulphide dissolve much sulphur and on evaporation can then be made to yield slightly impure lithium disulphide, but no higher polysulphide could be isolated. Thus it appears that the polysulphides of the alkali metals become less stable and more difficult to prepare with decreasing atomic weight of the metal.[33]

A phase-rule investigation of the systems formed by potassium cyanide with water and each of the cyanides of univalent copper, silver, gold, and thallium at 25° confirms the existence of several known compounds and shows that the new compounds $K_3Ag(CN)_4,H_2O$, $KAg_2(CN)_3,H_2O$, and $KTl(CN)_2$ also exist in the appropriate systems.[34]

In determining the compressibilities of certain alkali halides, it has been observed that freshly-fused rubidium bromide and iodide and cæsium bromide undergo a permanent contraction in volume of about 1%, this change occurring rapidly under high pressure and slowly on standing under ordinary conditions.[35]

Cuprous oxide, whether that formed by the action of nitrogen peroxide on copper or the anhydrous ignited crystalline materal, when treated with nitrogen peroxide in the cold takes up about 30% by weight of that gas without change in appearance, evolution of heat, or other sign of chemical change. The product dissociates completely on heating, without reduction of the nitrogen peroxide: it reacts violently with water, yielding nitric oxide and a solution of cupric nitrate with a little nitrite, probably through the reactions: (i) $2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$; (ii) $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$; (iii) $3Cu_2O + 14HNO_3 \longrightarrow 6Cu(NO_3)_2 + 2NO + 7H_2O$.

[30] K. Peters, *Z. anorg. Chem.*, 1924, **131**, 140; *A.*, ii, 174.

[31] *Ann. Report*, 1922, **19**, 41.

[32] G. F. Hüttig and F. Pohle, *Z. anorg. Chem.*, 1924, **138**, 1; G. F. Hüttig and F. Renscher, *ibid.*, **137**, 155; *A.*, ii, 676, 756.

[33] J. S. Thomas and J. H. Jones, *J.*, 1924, **125**, 2207.

[34] H. Bassett and A. S. Corbet, *ibid.*, p. 1660.

[35] T. W. Richards and E. P. R. Saerens, *J. Amer. Chem. Soc.*, 1924, **46**, 934; *A.*, ii, 408.

At 65—70°, the whole of the nitrogen peroxide is removed from this association with cuprous oxide by an inert solvent, such as carbon tetrachloride, leaving a residue of cuprous oxide. Hence it is concluded that the peroxide is adsorbed by, and not chemically combined with, the cuprous oxide.[36]

Some interesting work on the formation of silver nitride from silver ammonium fluoride and on the conditions of formation of fulminating silver from solutions of silver oxide in ammonia deserves mention, but cannot well be summarised.[37]

By a repetition and extension of work previously reported,[38] Hartung, using two Steele-Grant microbalances, one carrying 105 mg. and the other 43 mg. and both sensitive to 2×10^{-5} mg., and an apparatus improved in several important respects, has shown that by insolating thin films of silver bromide on flat silica supports in evacuated vessels containing a suitable halogen absorbent, preferably metallic copper, more than 96% of the bromine may be expelled. Investigation of the rate of bromination of thin silver films gives no evidence of the formation of silver sub-bromides, and there seems no reason to doubt that the production of a latent image when silver halides are illuminated for very short periods is due to incipient decomposition into silver and bromine of the type here studied.[39]

An *X*-ray analysis of a sample of purple of Cassius gives clear indication of the presence of crystalline gold and stannic oxide and confirms the view that this substance is merely a mixture of colloidal gold and colloidal stannic acid.[40]

Brief reference may be made to the reported formation of gold from mercury in mercury-vapour arc lamps.[41] Although atomic disruption is not necessarily involved,[42] the observation must await further confirmation, especially as the reported formation of helium from tungsten [43] cannot be verified by other observers.[44]

[36] J. R. Park and J. R. Partington, *J.*, 1924, **125**, 72; J. R. Partington, *ibid.*, p. 663; *A.*, ii, 183, 340.

[37] L. J. Olmer and Dervin, *Bull. Soc. chim.*, 1924, [iv], **35**, 152; L. J. Olmer, *ibid.*, pp. 333, 847; *A.*, ii, 410, 679.

[38] *Ann. Report*, 1922, **19**, 43.

[39] E. J. Hartung, *J.*, 1924, **125**, 2198.

[40] A. Huber, *Physikal. Z.*, 1924, **25**, 45; *A.*, ii, 229.

[41] A. Miethe, *Naturwiss.*, July 18, 1924. For methods used in estimating gold, see A. Miethe and H. Stammreich, *Z. anorg. Chem.*, 1924, **140**, 368; *A.*, ii, 874.

[42] F. Soddy, *Nature*, 1924, **114**, 244; *A.*, ii, 684.

[43] *Ann. Report*, 1922, **19**, 39.

[44] Sinclair Smith, *Proc. Nat. Acad. Arts Sci.*, 1924, **10**, 4; S. K. Allison and W. D. Harkins, *J. Amer. Chem. Soc.*, 1924, **46**, 814; *A.*, ii, 407; confirmed by a series of experiments made in the Reporter's laboratory; H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson, *J.*, 1925, **127**, 240.

Group II.

Calcium oxide reacts with nitrogen peroxide at all temperatures up to 400°, giving calcium nitrate and nitrite, nitric oxide and nitrogen. The free nitrogen arises from the oxidation of calcium nitrite to nitrate by the peroxide, which may occur in the following ways: (i) $Ca(NO_2)_2 + 2NO_2 \longrightarrow Ca(NO_3)_2 + 2NO$; (ii) $2Ca(NO_2)_2 + 2NO \longrightarrow 2Ca(NO_3)_2 + N_2$. Thus a loss of nitrogen may occur (for example, in nitrogen fixation processes using lime as an absorbent) to the extent of 5% of that originally present as peroxide. Calcium nitrite is not oxidised by oxygen below the temperature (230°) at which it begins to decompose according to the scheme: $Ca(NO_2)_2 \longrightarrow CaO + NO + NO_2$. The existence of the compound $Ca(NO_3)_2,4H_2O$ was confirmed.[45]

At temperatures above 1100°, calcium carbide dissociates into its elements: this dissociation is the first stage in the formation of calcium cyanamide, which is believed to occur by way of the following reactions: (i) $3CaC_2 \longrightarrow 3Ca + 6C$; (ii) $3Ca + N_2 \longrightarrow Ca_3N_2$; (iii) $Ca_3N_2 + 3C + 2N_2 \longrightarrow 3CaCN_2$. Calcium chloride accelerates the decomposition of calcium carbide and its favourable influence in the cyanamide process is hereby explained.[46]

Metallic barium and strontium, prepared according to the method of Guntz [47] by reducing with coarse aluminium powder a mixture of the oxide with 10% of peroxide, when redistilled from a small resistance furnace contained in an evacuated glass vessel, yielded very pure samples of these elements (about 20 g. of each, containing less than 0·1% of impurity). Both metals are silver-white, crystalline, and as soft and malleable as sodium; barium is spontaneously inflammable in moist air or hydrogen and tarnishes rapidly in pure, dry carbon dioxide; strontium is but little less reactive.[48] Less pure specimens of metallic strontium have been prepared by reducing the oxide with silicon or high-grade ferrosilicon at 1250°.[49]

In the absence of oxygen, zinc oxide is not reduced by carbon at 1000°, but a small quantity of oxygen causes reduction at a much lower temperature. Reaction between carbon monoxide and zinc oxide begins at 420° and it is to this action that the reduction by carbon under ordinary conditions is due.[50]

[45] J. R. Partington and F. A. Williams, *J.*, 1924, **125**, 947.

[46] H. J. Krase and J. Y. Yee, *J. Amer. Chem. Soc.*, 1924, **46**, 1358; *A.*, ii, 758; but compare O. Ruff and E. Foerster, *Z. anorg. Chem.*, 1923, **131**, 321; *A.*, ii, 256.

[47] A. Guntz, *Ann. Chim. Phys.*, 1905, [viii], **4**, 5; 1907, **10**, 437; *Bull. Soc. chim.*, 1906, [iii], **35**, 503.

[48] P. S. Danner, *J. Amer. Chem. Soc.*, 1924, **46**, 2382.

[49] C. Matignon, *Compt. rend.*, 1923, **177**, 1116; *A.*, ii, 44.

[50] A. d'Hooghe, *Bull. Acad. Roy. Belg.*, 1923, **9**, 323; *A.*, ii, 611.

The primary product of the interaction of mercury and nitric acid is mercurous nitrite. The yield of this salt is highest with 26% nitric acid at 30°, is increased by the presence of mercurous or ferric nitrate, and is reduced to zero if sodium nitrite or urea is added to the nitric acid or if the temperature rises above 52°. Ferrous sulphate reduces nitric acid to nitrous acid and thus accelerates the solution of mercury in the acid.[51]

Group III.

A new hydride of boron, formulated as $B_5H_{>9}$ and probably B_5H_{10}, has been found among the products formed on heating tetraborane, B_4H_{10}.[52] The new hydride cannot be separated from B_5H_9 by fractional distillation or condensation, but its presence is shown by the marked depression of the freezing point of B_5H_9; it decomposes rapidly at the ordinary temperature (B_5H_9 can thus be freed from it by keeping), yielding hydrogen and a non-volatile, yellow hydride insoluble in carbon disulphide but soluble in water and probably identical with the yellow decomposition product of B_6H_{10} described previously.

It is now found that the hydride B_5H_9 combines additively with ammonia at the ordinary temperature to form the compound $B_5H_9(NH_3)_4$: this compound, treated with hydrogen chloride, yields at first $B_5H_5Cl_4(NH_3)_4$ and by prolonged action $B_5H_2Cl_7(NH_3)_4$, and this substituted ammine, dissolved in water, yields hydrogen and a strongly reducing solution giving a characteristic precipitate with sulphates. A second new hydride, B_5H_{11}, has been isolated from the decomposition products of diborane; it is a colourless, mobile liquid which does not solidify at — 110° and rapidly decomposes at the ordinary temperature, yielding hydrogen and the solid hydride $B_{10}H_{14}$, m. p. 99·5°.[53]

Thermal investigation of the ternary alloy system Al–Cd–Zn shows that the chief feature of the *liquidus* surface is a deep valley joining almost linearly the eutectics at 94·4% Zn and 380° and at 17·4% Zn and 268° in the Zn–Al and Zn–Cd series, respectively.[54]

Specimens of the hydroxides of aluminium, chromium, and zinc, prepared in various ways and of various ages up to 4 years, were examined by the Debye-Scherrer method of *X*-ray analysis with the following results. At the ordinary temperature, gelatinous aluminium hydroxide slowly changes into crystalline hydrargillite, but the freshly-precipitated substance, when heated at 100° for

[51] C. C. Palit and N. R. Dhar, *Z. anorg. Chem.*, 1924, **134**, 191; *A.*, ii, 486.
[52] *Ann. Report*, 1923, **20**, 38.
[53] A. Stock and W. Siecke, *Ber.*, 1924, **57**, [*B*], 562; *A.*, ii, 405
[54] N. F. Budgen, *J.*, 1924, **125**, 1642.

some time, tends to form microcrystalline bauxite : zinc hydroxide, air-dried at the ordinary temperature, is partly crystalline and becomes more so by ageing : chromium hydroxide, even when aged, shows no sign of crystalline structure.[55]

Solutions of aluminium chloride in carbonyl chloride react with many metals, forming double salts which, in the case of calcium and magnesium, are soluble and do not impede the action by coating the metal. From the solution obtained with calcium, a compound, $CaCl_2,2AlCl_3,3COCl_2$, has been isolated; it readily loses carbonyl chloride (dissociation pressure 25 mm. at 19·5°) and on heating loses aluminium chloride to form the known compound $3CaCl_2,4AlCl_3$.[56]

Aluminium chloride and sulphur chloride unite to form a compound, $AlCl_3,3S_2Cl_2$, which on chlorination yields $AlCl_3,SCl_2$ and $AlCl_3,SCl_4$ and combines with sulphur to form $AlCl_3,2S_3Cl_2$ and $AlCl_3,2S_4Cl_2$. All these compounds are red, uncrystallisable liquids, insoluble in sulphur chloride. On extraction with carbon disulphide, the last two lose sulphur chloride and leave solid residues, $AlCl_3,2S_2$ and $AlCl_3,S_2$, which react with water, depositing sulphur but yielding no hydrogen sulphide. It is hence concluded that they are co-ordination compounds of aluminium chloride with the polythiochlorides, S_3Cl_2 and S_4Cl_2, the presence of which in solutions of sulphur in sulphur chloride is postulated to account for the observed changes in boiling point with increasing sulphur content in such solutions.[57]

The system thallic oxide–sulphur trioxide–water yields two compounds only, $HTl(SO_4)_2,4H_2O$ and $OH{\cdot}TlSO_4,2H_2O$, both stable only in strongly acid solutions and readily hydrolysed by water. The changes in transition temperature between these salts with acid concentration have been determined : at 25° the basic salt is in equilibrium with acid concentrations from 10—40% and the acid salt with concentrations from 42—75% : thallic oxide does not dissolve in more concentrated acid. It is supposed that the heptahydrated normal salt described by Crookes and by Strecker must have been a molecular mixture of the two salts now found. Analogous thallic selenates, $HTl(SeO_4)_2,2H_2O$ and $OHTlSeO_4,H_2O$, are found to be the only selenates capable of separate existence and they closely resemble the sulphates in their solubility relations and in their sensitiveness to water.

[55] R. Fricke and F. Wever, *Z. anorg. Chem.*, 1924, **136**, 321; *A.*, ii, 616; compare R. Willstätter and H. Kraut, *Ber.*, 1924, **57**, [*B*], 1082; *A.*, ii, 615.

[56] A. F. O. Germann and K. Gagos, *J. Physical Chem.*, 1924, **28**, 965; *A.*, ii, 861.

[57] O. Ruff and H. Golla, *Z. anorg. Chem.*, 1924, **138**, 17, 33; *A.*, ii, 672, 684.

Thallic hydroxide dissolves in a saturated solution of ammonium sulphate, and from this solution at 0° addition of ammonia and alcohol precipitates a compound, $Tl_2(SO_4)_3,12NH_3,12H_2O$, stable only in an atmosphere of ammonia: a similar selenium compound was also isolated. A colourless thallo–thallic selenate,

$$Tl_2SeO_4,Tl_2(SeO_4)_3;$$

a yellow double salt, $5Tl_2SeO_4,Tl_2(SeO_4)_3$, analogous to the known double sulphate, and certain other salts containing both halogen and the sulphate or selenate radical have been prepared.[58]

By examination of the arc spectra and *X*-ray spectra of neodymia–samaria fractions of rare-earth material, search has been made for the element of atomic number 61, but without success.[59]

Normal carbonates of cerium, lanthanum, neodymium, and praseodymium, of the type $E_2O_3,3CO_2,8H_2O$, are obtained by precipitating 2% solutions of the chlorides with a solution of sodium hydrogen carbonate saturated with carbon dioxide. They are at first amorphous, but rapidly become crystalline, and when air-dried have the formula given above; drying in a vacuum over sulphuric acid produces the dihydrate; drying at 100° yields the monohydrate; prolonged heating at 200° in carbon dioxide removes the remaining water and yields the anhydrous normal carbonates. When heated with excess of water, the carbonates lose one-third of their carbon dioxide, forming basic carbonates of the type $OH{\cdot}E{\cdot}CO_3$. The normal carbonates, heated in an atmosphere of carbon dioxide, are stable up to 300° and thereafter lose carbon dioxide, rapidly at 400°, all except cerous carbonate forming the basic carbonate, E_2O_3,CO_2, stable at a high temperature (La, 900°; Pr, 815°; Nd, 800°). Above these temperatures, the lanthanum and praseodymium compounds are rapidly converted into oxides: the neodymium compound is first converted into $Nd_2O_3,\frac{1}{2}CO_2$, stable up to 870°, and then yields the oxide. The decomposition of cerous carbonate is complicated by the intermediate formation of the ceric compounds, $Ce_2O_4,3CO_2$ and $Ce_2O_4,\frac{1}{2}CO_2$, which at 900° yield ceric oxide.[60]

Work published on the complex sulphates of quadrivalent cerium, on double sulphites of the alkalis with cerium, lanthanum, and didymium, and on the chromates of lanthanum, praseodymium, neodymium, and samarium cannot usefully be summarised.[61]

[58] J. Meyer and H. Wilk, *Z. anorg. Chem.*, 1923, **132**, 239; *A.*, ii, 259.

[59] L. F. Yntema, *J. Amer. Chem. Soc.*, 1924, **46**, 37; W. Prandtl and A. Grimm, *Z. anorg. Chem.*, 1924, **136**, 283; *A.*, ii, 185, 615.

[60] J. Preiss and A. Dussik, *ibid.*, 1923, **131**, 275; J. Preiss and N. Rainer, *ibid.*, p. 287; *A.*, 1924, ii, 261, 262.

[61] V. Cuttica, *Gazzetta*, 1923, **53**, 761, 769; H. T. S. Britton, *J.*, 1924, **125**, 1875; *A.*, ii, 112, 113.

An investigation of pure praseodymia prepared by basic precipitation [62] confirms the curious fact that the composition of this oxide conforms almost exactly to the composition Pr_6O_{11}.[63]

A study of the effect of mixtures of ceria and thoria on the combination of hydrogen and oxygen at 450° shows that their catalytic activity exactly parallels their light-giving powers in the incandescence mantle in that it is a maximum for the mixture containing 1% of ceria and is the same for pure thoria as for the mixture containing 9% of ceria.[64]

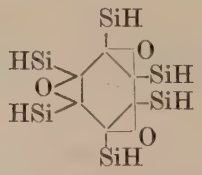
Group IV.

The relationship of rate of loss of weight of pure carbon filaments to the temperature at which they were heated in a helium atmosphere at known pressure, and certain other observations, indicate, although they cannot prove, that carbon has a vapour pressure of about 1 mm. at 2400°.[65]

X-Ray analysis of thirty-four different forms of "amorphous" carbon establishes their essential identity with each other and with graphite,[66] and measurements of the real density of various charcoals are held to indicate that they all consist of graphite contaminated with hydrocarbons.[67]

Carbon monoxide is readily absorbed by a solution of silver sulphate in sulphuric acid, the rate of absorption increasing with the concentration of the acid: in a vacuum, the gas is again liberated in a manner dependent on the temperature.[68]

Further investigation of the compound formerly called "oxydisilin" and formulated as $Si_2H{\cdot}OH$,[69] obtained by the action of dilute hydrochloric acid on calcium silicide,[70] has afforded evidence that it has the constitution formulated below, and it is renamed "*siloxen*."



[62] W. Prandtl and K. Huttner, *Z. anorg. Chem.*, 1924, **136**, 289; *A.*, ii, 615.
[63] P. M.-P. Brinton and Pagel, *J. Amer. Chem. Soc.*, 1923, **45**, 1460.
[64] R. L. Swan, *J.*, 1924, **125**, 780.
[65] A. Thiel and F. Ritter, *Z. anorg. Chem.*, 1923, **132**, 125; *A.*, ii, 253.
[66] G. Asahara, *Japan J. Chem.*, 1922, **1**, 35; *A.*, ii, 172.
[67] H. C. Howard and G. A. Hulett, *J. Physical Chem.*, 1924, **28**, 1082; *A.*, ii, 823.
[68] W. Manchot *et alii*, *Ber.*, 1924, **57**, [*B*], 1157; *A.*, ii, 609.
[69] H. Kautsky, *Z. anorg. Chem.*, 1921, **117**, 209; *A.*, 1921, ii, 505.
[70] H. Kautsky and G. Herzberg, *Z. angew. Chem.*, 1923, **36**, 508.

The bromine derivative (formerly described as " silical bromide ") and an iodine derivative now obtained are $Si_6H_3O_3Br_3$ and $Si_6H_3O_3I_3$. Tribromosiloxen, when treated with bromine sufficient to form hexabromosiloxen, absorbs it completely and is converted into a yellow solid readily hydrolysed to a black hydroxy-derivative; greater proportions of bromine are also absorbed, but to form colourless compounds which yield colourless hydration products: hence it is inferred that siloxen contains six hydrogen atoms similarly united to silicon. Siloxen, when exhaustively chlorinated, yields hexachlorodisiloxan, $SiCl_3{\cdot}O{\cdot}SiCl_3$, and when treated with methyl alcohol and ammonia yields hexamethoxydisiloxan, $O[Si(OMe)_3]_2$, hence the oxygen atoms are believed to be directly linked each to two silicon atoms.[71] Various other reactions of these compounds are described in the papers cited.

A silicon analogue of calcium cyanamide, $CaSiN_2$, is formed, together with calcium silicocyanide and silicon, by interaction between nitrogen and calcium disilicide, at 1150°, thus:

$$2CaSi_2 + 2N_2 \longrightarrow CaSiN_2 + Si + Ca(SiN)_2.$$

The reaction is greatly accelerated by the presence of calcium chloride or of less than 5% of calcium fluoride, and then occurs at as low a temperature as 850°. Neither the silicocyanamide nor the silicocyanide could be isolated from the reaction product, but both dissolved in hydrochloric acid without separation of silica.[72]

A relatively large amount of germanium has been extracted from germanite, from Tsumeb, S.W. Africa, which contains 5·1% of germanium and 0·57% of gallium. Metallic germanium was prepared by reducing the dioxide with potassium cyanide and charcoal.[73]

Important work has been published on the hydrides of germanium.[74] When heated at about 500° in hydrogen, powdered germanium (3 parts) reacts with arsenic-free magnesium turnings (2 parts) with evolution of much heat, the mass glowing brightly, to form dark-grey, granular magnesium germanide. By slowly adding dilute hydrochloric acid to this compound in a flask filled with pure hydrogen, a gaseous mixture of germanium hydrides with hydrogen was obtained containing about 23% of the total germanium used. This mixture was separated and the constituents were examined by means of an apparatus (the construction and use of which are described in detail in the original) similar to that used

[71] H. Kautsky and G. Herzberg, *Ber.*, 1924, **57**, [*B*], 1665; H. Kautsky and H. Thiele, *Z. angew. Chem.*, 1924, **37**, 540; *A.*, ii, 852, 674.

[72] L. Wöhler and O. Bock, *Z. anorg. Chem.*, 1924, **134**, 221; *A.*, ii, 473.

[73] J. S. Thomas and W. Pugh, *J.*, 1924, **125**, 816.

[74] L. M. Dennis, R. B. Corey, and R. W. Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657; *A.*, ii, 343.

by Stock for the study of the hydrides of silicon.[75] To test this apparatus, Stock's work on the isolation, analysis, and determination of physical constants of pure monosilane and disilane was repeated and confirmed in all details. Fractional distillation and condensation of the germanium hydrides yielded three fractions consisting of monogermane, GeH_4, digermane, Ge_2H_6, and trigermane, Ge_3H_8, and a small amount of liquid residue which probably contained higher hydrides. Of the total amount of germanium obtained as hydrides, 73·6% was present as monogermane, 22% as digermane, and 1% as trigermane. The identity of the hydrides was proved by analysis (by thermal decomposition into germanium and hydrogen) and by determinations of gaseous density. Monogermane has already been described.[76]

Digermane is a colourless liquid, m. p. — 109°, b. p. 29°, $d^{-109°}$ 1·98; its vapour-pressure curve was plotted from — 98° to + 30°. Trigermane is also a liquid, m. p. — 105·6°, b. p. 110·5°, $d^{-105·6°}$ 2·20; its vapour-pressure curve was determined from 2·4° — 111·5°. Thermal dissociation at a pressure of 200 mm. begins with digermane at 214—218° and with trigermane at 194°; in the latter case, a small quantity of a clear, colourless liquid of high b.p., possibly a polymerised unsaturated hydride, was formed in small quantity.

When exposed to air, digermane turns yellow, then light brown, and finally yields a dark brown solid; it is not ordinarily spontaneously inflammable, but readily ignites and burns vigorously, leaving a residue streaked white and black and brown. The action of oxygen on digermane in one case caused spontaneous inflammation; usually no action occurs at first, but after 10 minutes the liquid deposits a white solid which after a time turns yellow. Trigermane behaves in a very similar way with air and oxygen.

Liquid digermane is immiscible with water, but reacts after a time to produce a white, gelatinous solid which gradually turns yellow and then light brown, a gas being evolved at the interface between the liquids. With 33% sodium hydroxide solution, liquid digermane, unlike monogermane and trigermane, reacts to produce a colourless, combustible gas, although in insufficient quantity for identification. Both digermane and trigermane dissolve in carbon tetrachloride with evolution of heat, forming a clear solution which deposits a white solid on exposure to air.[74]

When an aqueous solution of germanium dioxide is evaporated and the residue is heated to any temperature between 225° and 1100°, part of the oxide is insoluble in water and very inert toward

[75] A. Stock and K. Somieski, *Ber.*, 1916, **49**, 111; *A.*, 1916, ii, 319.
[76] *Ann. Report*, 1923, **20**, 43.

acids and alkalis. The yield of insoluble is highest when the residue is heated to 380°, but the mode of increase of this yield with duration of heating is such as to indicate that it can never exceed a certain small value, *e. g.*, about 15% at 280°. All specimens of the oxide melt between 1090° and 1100° to a viscous liquid which solidifies to a colourless glass, readily and completely soluble in boiling water. Therefore it seems probable that germanium dioxide exists in two or more allotropic modifications.[77]

Further investigation of zirconium minerals has confirmed the fact that hafnium is always associated with zirconium, although, in general, minerals rich in zirconium are poor in hafnium, whilst those poor in zirconium and containing a large quantity of rare-earths are rich in hafnium : thortveitite from Madagascar contains 3·2% HfO_2 and only 2% ZrO_2, and a Norwegian thortveitite similarly showed a high proportion of hafnium.[78] The foregoing generalisation is supported by the finding that zirconium from various minerals has an atomic weight which is higher when the content of rare-earths is high.[79] Examination of the optical spectrum of hafnium shows that many of the strong hafnium lines have previously been recorded as weak spark lines of zirconium.[80]

Zirconia prepared from the normal sulphate by ignition at 1000° has $d^{20°}$ 5·73, whilst hafnia similarly prepared and containing less than 0·5% ZrO_2 has $d^{20°}$ 9·67. These values are constant and reproducible provided that the method of preparation of the oxide is the same; hence the considerable difference between them affords a convenient and accurate means of determining the proportions of zirconia and hafnia in mixed oxides, the percentage of hafnia being given by $d - 5{\cdot}73/0{\cdot}0394$, where d is the density at 20° of the mixed oxide prepared as described above.[81]

Anomalies in a previous investigation of the atomic weight of zirconium are now definitely traced to a small and varying content of hafnium in the material used.[82]

Work on the stannic acids, which cannot be described in detail here, is held to afford evidence that unstable but definite monostannic acids can exist of the type $Sn(OH)_6H_2$, $Sn(OH)_4$, or $SnO(OH)_2$.[83]

[77] J. H. Müller and H. R. Blank, *J. Amer. Chem. Soc.*, 1924, **46**, 2358.

[78] G. von Hevesy and V. T. Jantzen, *Chem. News*, 1924, **128**, 341; *Z. anorg. Chem.*, 1924, **133**, 113, 387; *A.*, ii, 492, 571, 620.

[79] E. Urbain and G. Urbain, *Compt. rend.*, 1924, **178**, 265; *A.*, ii, 194.

[80] H. M. Hansen and S. Werner, *Nature*, 1923, **112**, 900; *A.*, ii, 79.

[81] G. von Hevesy and V. Berglund, *J.*, 1924, **125**, 2372.

[82] F. P. Venable and J. M. Bell, *J. Amer. Chem. Soc.*, 1924, **46**, 1833; *A.*, ii, 690.

[83] R. Willstätter, H. Kraut, and W. Fremery, *Ber.*, 1924, **57**, [*B*], 63, 1491; *A.*, ii, 266, 767.

Lead tetrachloride purified by distillation in a high vacuum dissolves in benzene and its homologues to give deep brownish-red solutions which, if dilute, may be kept without change for several hours in the dark, but if concentrated decompose with explosive violence after some little time. The brown colour of the solutions is discharged by addition of carbon tetrachloride, chloroform, ethylene dibromide, acetic acid, or ether, without deposition of lead dichloride.[84]

Interaction of lead salts and disodium hydrogen phosphate in aqueous solution at the ordinary temperature yields at first tertiary lead phosphate, $Pb_3(PO_4)_2$, but by prolonged contact with the solution this is converted into the secondary salt, $PbHPO_4$, which is the equilibrium product, stable over a wide range of concentration of phosphoric acid (0 — 49% P_2O_5 at 25°). With higher concentrations of acid, the primary phosphate, $PbH_4(PO_4)_2$, is the stable solid phase.[85]

Group V.

Pure ammonia, containing only a trace of hydrogen as impurity, may be obtained by allowing pure calcium or magnesium nitride to fall into water. Commercial ammonium salts always contain organic matter, corresponding with about 0·5% of carbon in the samples examined, but this can be destroyed by oxidation with nitric acid or permanganate at high temperatures and the residual salt will yield pure ammonia by the usual methods.[86]

Dry mixtures of ammonia with electrolytic gas become explosive when the ratio of electrolytic gas to ammonia is slightly greater than 1, 79% of the ammonia being then decomposed; when this ratio is a little higher than 3, the ammonia is wholly decomposed, the gaseous products containing only steam, hydrogen, and nitrogen. Explosion of ammonia with a deficiency of oxygen causes complete decomposition of the excess of ammonia, oxides of nitrogen being formed only if the ratio of ammonia to oxygen is less than 1·6. When oxides of nitrogen are so formed, the proportion of nitrogen oxidised is greater than in the explosion of a corresponding mixture of nitrogen, hydrogen, and oxygen.[87]

Equilibrium values for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ have been determined, first for the range 10—100 atms., and 325—500°, and later for the range 300—1000 atms., and the temperatures 450°, 475°, and 500°, and show that at 1000 atms. and 450° the proportion of ammonia at equilibrium is 69·4%.[88]

[84] E. Krause, *Ber.*, 1924, **57**, [*B*], 318; *A.*, ii, 259.

[85] L. T. Fairhall, *J. Amer. Chem. Soc.*, 1924, **46**, 1593; *A.*, ii, 612.

[86] L. Moser and R. Herzner, *Monatsh.*, 1923, **44**, 115.

[87] J. R. Partington and A. J. Prince, *J.*, 1924, **125**, 2018.

[88] A. T. Larson and R. L. Dodge, *J. Amer. Chem. Soc.*, 1923, **45**, 2918; A. T. Larson, *ibid.*, 1924, **46**, 367; *A.*, ii, 331.

A catalyst, "nitroxan," consisting of an equimolecular mixture of barium metaplumbate and barium manganate is able to effect complete oxidation of ammonia to nitric acid, which, at temperatures below 450°, is retained by the catalyst as barium nitrate. This nitrate may be removed by lixiviation and replaced by barium hydroxide to regenerate the catalyst.[89]

By the action of amalgamated aluminium on a solution of potassamide in liquid ammonia, potassium ammonoaluminate, $Al(NH_2)_3,KNH_2$, is obtained; it crystallises in colourless needles and resembles the sodium salt previously described.[90] When heated to 50° in a vacuum, it yields a white, non-crystalline substance, $Al(NH_2)_2{\cdot}NHK$.

Potassium ammonomanganite, $Mn(NHK)_2,2NH_3$, is obtained by the slow action of metallic manganese on a solution of potassamide in liquid ammonia, or, more readily, by interaction of potassamide and manganous thiocyanate in this solvent; it forms cream-coloured crystals which oxidise rapidly in air and are vigorously hydrolysed by water. If the manganous thiocyanate is in excess, impure manganous amide, $Mn(NH_2)_2$, is obtained.[91]

Improved methods are described for the preparation of hyponitrites,[92] and the mechanism of the thermal decomposition of salts of hydroxylamine and hydrazine and of the oxidation of hydrazine has been investigated.[93]

Interesting work has been done on the oxidation of phosphorus. The statement that a blast of air can detach the luminosity from phosphorus and cause it to move down-stream [94] is confirmed and it is shown that inhibitors, *e.g.*, carbon disulphide, have no effect when introduced into the glow, but extinguish it when introduced on the up-stream side between the glow and the phosphorus. The velocity of blast necessary to detach the glow from the phosphorus varies enormously with temperature and oxygen concentration, being less the higher the oxygen content of the blast and the lower the temperature. This velocity is evidently a measure of the rate of propagation of the glow, which therefore appears to be due to an oxidation of the vapour of phosphorus or oxides of phosphorus catalysed by the products of combustion. The known extinction of the glow is thus seen to be the limiting case of slow propagation,

[89] G. Kassner, *Z. angew. Chem.*, 1924, **37**, 373; *A.*, ii, 604.

[90] *Ann. Report*, 1923, **20**, 48.

[91] F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1924, **46**, 1545; *A.*, ii, 607.

[92] L. W. Jones and A. W. Scott, *ibid.*, p. 2172; E. Weitz and W. Vollmer, *Ber.*, 1924, **57**, [*B*], 1015; *A.*, ii, 850, 608.

[93] K. A. Hofmann and F. Kroll, *Ber.*, 1924, **57**, [*B*], 937; E. J. Cuy, *et alii*, *J. Amer. Chem. Soc.*, 1924, **46**, 1786, 1796, 1810; *A.*, ii, 545, 672, 673.

[94] L. and E. Bloch, *Compt. rend.*, 1908, **147**, 842; *A.*, 1908, 1032.

and the extinction by inhibiting substances such as carbon disulphide, turpentine, or oxygen, is interpreted as a case of catalyst poisoning. In dry oxygen, similar phenomena are observed, save that the glow persists at all ordinary temperatures but is sharply extinguished at a lower temperature, about $-20°$.[95] Further experiments have now shown conclusively that, as would appear from the foregoing observations, the oxidation of phosphorus by moist oxygen occurs slowly even when there is no visible glow, and that this "dark" reaction is a volume reaction occurring in the vapour phase and not a surface action. If phosphorus is confined in oxygen at, say, 15°, and the pressure is reduced, the glow begins sharply at a certain definite pressure. If the pressure is then first slightly increased (thus extinguishing the glow) and then again lowered without delay, the glow begins at a slightly higher pressure than in the first case, as if some kind of initial resistance to glowing had been broken down. This resistance is recovered if the extinction of the glow is maintained for a minute or more. By taking advantage of this curious fact, it is possible to arrange that at a given temperature and pressure in the same gas the phosphorus may either glow or remain dark: oxidation occurs in either case, but at very different rates, the time required for the absorption of a given volume of oxygen being about 145 times greater when the phosphorus is dark than when it is glowing.[96]

The spectrum of the flame of phosphorus, whether burning in air enriched with oxygen or in air at reduced pressure, shows series of bands in the same position, but in the latter case resolved into smaller bands identical with those observed in the glow of phosphorus.[97] It has further been shown that the amount of ozone formed during the oxidation of phosphorus is proportional to the intensity of the glow and, what is more important, that the glow of phosphorus or of phosphorous oxide can ozonise oxygen and ionise air separated from the glowing material by a window of quartz or fluorite 2 mm. thick.[98] Considering all these facts in relation to previous knowledge (which is well summarised in the paper last cited), there is evidently strong reason to believe that the cold oxidation of phosphorus first produces phosphorous oxide, the further oxidation of the latter under appropriate conditions emitting both the visible glow and light of very short wave-length which causes the observed production of ozone and gaseous ions.

[95] Lord Rayleigh, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 322; *A.*, 1923, ii, 755.
[96] *Idem*, *ibid.*, 1924, [*A*], **106**, 1; *A.*, ii, 605; see also K. R. Krishna Iyer, *Chem. News*, 1923, **127**, 321; *A.*, ii, 39.
[97] H. J. Emeléus and W. E. Downey, *J.*, 1924, **125**, 2491.
[98] W. E. Downey, *ibid.*, p. 347.

Oxidation of hypophosphorous acid by chromic acid proceeds by a reaction which is unimolecular with regard to each reactant, does not involve hydrogen ions, and may be represented as occurring in two stages :

$$H_3PO_2 + Cr_2O_7'' \longrightarrow H_3PO_3 + Cr_2O_6'';$$
$$2H_3PO_2 + Cr_2O_6'' + 8H^{\cdot} \longrightarrow 2H_3PO_3 + 2Cr^{\cdot\cdot\cdot} + 4H_2O;$$

of which the first only is measurable. This reaction thus gives no information as to the existence of an active form of the acid.[1] On the other hand, the interaction of phosphorous acid with mercuric chloride affords confirmatory evidence of the existence of a second, active form of this acid.[2]

The conditions of formation of various orthophosphates of lithium, magnesium, zinc, and beryllium have been defined and some new salts isolated, *viz.*, lithium diammonium phosphate, $Li(NH_4)_2PO_4$; primary beryllium phosphate, $Be(H_2PO_4)_2$, and the double salt $2Be(H_2PO_4)_2,BeHPO_4$.[3]

In the course of experiments on the preparation of the hydride As_2H_2, a new arsenic hydride, As_4H_2, was obtained as a red, non-crystalline, insoluble solid, decomposing when heated to yield free arsenic, arsine, and hydrogen. It results from the oxidation of arsine by stannic chloride in presence of hydrochloric acid : it is unchanged by boiling water or hydrochloric acid, yields arsenic when treated with a boiling concentrated solution of alkali or fused alkali, and is oxidised to arsenic acid by nitric acid, bromine, or hydrogen peroxide.[4]

Arsenides of several metals (Cu_3As; Pb_3As_2; Hg_3As; AuAs; Ag_3As; BiAs; Cd_3As_2; Fe_3As_2; Ni_3As_2) have been prepared by dropping an aqueous solution of a salt of the metal into an atmosphere of arsenic trihydride free from air. They are black substances, readily oxidised in air to form the metal and arsenious acid, and igniting spontaneously when dry; at high temperatures in the absence of air, the arsenides of the noble metals are almost completely dissociated, whilst the others yield arsenic and a lower arsenide. Dilute acids and alkalis have no action on the arsenides of copper, gold, and bismuth, but liberate arsine from the arsenides of lead and cadmium.[5]

Reinvestigation of the supposed suboxide of bismuth shows that as prepared by heating the basic oxalate or reducing the hydroxide

[1] A. D. Mitchell, *J.*, 1924, **125**, 564.

[2] *Idem*, *ibid.*, p. 1013.

[3] Travers and (Mlle) Perron, *Ann. Chim.*, 1924, [x], **1**, 135, 298; *A.*, ii, 676, 677.

[4] L. Moser and A. Brukl, *Monatsh.*, 1924, **45**, 25; *A.*, ii, 851.

[5] A. Brukl, *Z. anorg. Chem.*, 1923, **131**, 236; *A.*, ii, 251.

it is of variable composition and contains less bismuth than corresponds with the formula BiO. Metallic bismuth can be extracted from the oxide by shaking it with mercury, and when heated in dry hydrogen sulphide for many hours it behaves as a mixture of metal, trioxide, and hydroxide, each of which reacts with the gas at a different rate. The heat of reaction with hydrochloric acid, the solubility in aqueous caustic soda, and the specific magnetic susceptibility for the supposed suboxide have values indistinguishable from those given by a mixture of bismuth (1 atom) and bismuth trioxide (1 mol.); hence it is concluded that the suboxide does not exist.[6]

Group VI.

The residual oxygen left on explosion of pure ozone or rich mixtures of ozone with oxygen contains much less ozone than it should in accordance with the Nernst heat theorem.[7] On the other hand, the silver test shows that flames of hydrogen, coal-gas, methane, ethylene, acetylene, carbon monoxide, and cyanogen contain quantities of ozone (0·1% in the oxyhydrogen flame at 1500° and 1% in the acetylene blowpipe flame) much too great to be accounted for solely by thermal formation according to the Nernst theorem. In the cases of carbon monoxide and cyanogen, the yield of ozone is not diminished by drying the gases, therefore it seems improbable that hydrogen peroxide plays any part in its formation.[8] If hydrogen, coal-gas, or acetylene is supplied to the inner jet and oxygen to the outer jet of a small blowpipe, and a small flame so formed is caused to impinge directly on a water-cooled silica tube, a considerable yield of ozone is obtained and its production may readily be demonstrated on the lecture table.[9]

Determinations of the vapour pressure curve for pure ozone from — 169° (4·8 mm.) to — 108·5° (840·8 mm.) indicate that the b. p. at 760 mm. is — 110·7°.[10]

Sulphur vapour shows a maximum absorption for light at about $\lambda = 2750$ Å., corresponding on the radiation theory with a critical increment of 51,760 cal. per gram-atom of sulphur, in close agreement with that calculated from the temperature coefficient of the thermal gaseous reaction between hydrogen and sulphur. In agreement with hypothesis, ultra-violet radiation of this wave-

[6] E. Neusser, *Z. anorg. Chem.*, 1924, **138**, 180, 313; *A.*, ii, 691, 559.

[7] E. H. Riesenfeld and M. Beja, *ibid.*, p. 245; *A.*, ii, 470; compare H. v. Wartenburg and B. Sieg, *Ber.*, 1920, **53**, [*B*], 2192; *A.*, 1921, ii, 107.

[8] W. Manchot and E. Bauer, *Z. anorg. Chem.*, 1924, **133**, 341; *A.*, ii, 543.

[9] K. A. Hofmann and P. Kronenberg, *Ber.*, 1924, **57**, [*B*], 1200; *A.*, ii, 603.

[10] E. H. Riesenfeld and M. Beja, *Z. anorg. Chem.*, 1923, **132**, 179; *A.*, ii, 248.

length was found to be active in initiating a photochemical reaction between hydrogen and sulphur vapour proportional to the pressure of the latter. The conclusion drawn is that the activation of sulphur molecules may occur both by radiation and by collision, that in either case the energy of activation is constant, and hence that the latter case is amenable, not to the Newtonian laws of inelastic impact, but to those of quantum dynamics, the same amount of energy being extracted from the colliding molecules whatever the force of their impact, provided this exceeds a certain magnitude.[11]

A mixture of silver fluoride and sulphur heated in a vacuum yields a considerable volume of gas, having *V.D.* 97·3 and containing 64·04% S and 35·17% F and believed to be impure disulphur difluoride, S_2F_2. The gas is colourless, has an odour similar to but even more objectionable than that of sulphur chloride, and is immediately decomposed by moisture with deposition of sulphur.[12]

Pure sodium thiosulphate is readily obtained when sodium hydrosulphide (1 mol.) and sodium hydrogen sulphite (2 mols.) are mixed in aqueous solution; the reaction proceeds well also between sodium sulphide and sulphur dioxide or between sodium sulphite and hydrogen sulphide provided there is present sufficient sodium hydroxide to produce ultimately sodium hydrosulphide and bisulphite in the correct proportion. A mechanism for the reaction is suggested.[13]

The action of dry hydrogen sulphide on a suspension of lead thiosulphate in absolute alcohol yields an alcoholic solution of thiosulphuric acid which is stable for some time, but after a few days decomposes, giving sulphur and pentathionic acid. An aqueous solution of thiosulphuric acid, stable for about an hour at 15°, can be prepared by adding a little concentrated aqueous sodium thiosulphate to fuming hydrochloric acid.[14]

Pentathionic acid is formed by the action of sulphur dioxide on an aqueous suspension of sulphur according to the scheme: $5S + 5SO_2 + 2H_2O \longrightarrow 2H_2S_5O_6$. This reaction, together with the direct formation of tetrathionic acid in Wackenroder's solution, thus, $3SO_2 + H_2S \longrightarrow H_2S_4O_6$, can account for all the cases of formation of polythionic acids hitherto observed.[15]

None of the methods described in the literature for the preparation of pyrosulphates yields the pure salts; they can only be obtained by direct union of the sulphates with sulphur trioxide

[11] R. G. W. Norrish and E. K. Rideal, *J.*, 1924, **125**, 2070.
[12] M. Centnerszwer and C. Strenk, *Ber.*, 1923, **56**, [*B*], 2249; *A.*, ii, 167.
[13] F. Foerster and E. T. Mommsen, *ibid.*, 1924, **57**, [*B*], 258; *A.*, ii, 248.
[14] J. Casares Gil and J. Beato, *ibid.*, 1923, **56**, [*B*], 2451; *A.*, ii, 104.
[15] E. Josephy, *Z. anorg. Chem.*, 1924, **135**, 21; *A.*, ii, 470.

under anhydrous conditions. The acid sulphates cannot be completely dehydrated even under reduced pressure or in an atmosphere of sulphur trioxide. Sodium pyrosulphate is a white, crystalline solid, m. p. 400·9°, $d_4^{25°}$ 2·658, dissociating rapidly at 460° and deliquescing in moist air to sodium hydrogen sulphate. This salt, m. p. 185·7°, forms with the pyrosulphate a system showing a eutectic at 182·7° and 6·8 mol. % of pyrosulphate. Potassium pyrosulphate crystallises in transparent, colourless prisms, m. p. 414·2°, $d_4^{25°}$ 2·512, and on cooling changes at 315° to an opaque, porcelain-like mass and gives thermal indications of a second transformation at 225°. With potassium hydrogen sulphate, it forms a eutectic at 201·2° and 14 mol. % of pyrosulphate.[16]

Powdered tellurium heated in carbonyl chloride yields tellurium dichloride as a brown vapour condensing to a velvety black, crystalline solid which is decomposed by water to yield tellurium and the oxychloride $TeOCl_2$. By repeated sublimation with small quantities of ammonium chloride, the dichloride forms ammonium chlorotellurite, $(NH_4)_2TeCl_4$, as a greenish-black mass stable in air.[17]

Pure metallic chromium may be obtained by reducing chromic oxide at 1500° in perfectly dry hydrogen.[18]

A new salt of tervalent molybdenum, the oxysulphate $Mo_2O(SO_4)_2,xH_2O(x = 5 \text{ or } 6)$, is obtained by electrolytic reduction of a solution of molybdenum trioxide in sulphuric acid and can be isolated by pouring the electrolyte into acetone under exclusion of air. It is a green, hygroscopic solid, very readily hydrolysed and oxidised.[19] A number of double salts containing the chloride, bromide, or fluoride of tervalent molybdenum have also been described,[20] and much additional information has been published on the " dichlorides " of molybdenum, tungsten, and tantalum.[21]

Good deposits of very pure tungsten are formed by electrolysis of solutions of tungstic acid (1 part) in a fused mixture of sodium and potassium chlorides (not less than 2 parts). With higher proportions of tungstic acid in the electrolyte, various bronzes are produced.[22] Metallic uranium containing 99·9% U can be obtained

[16] L. Cambi and G. Bozza, *Ann. Chim. Applicata*, 1923, **13**, 221; *A.*, ii, 37.

[17] K. Lindner and L. Apolant, *Z. anorg. Chem.*, 1924, **136**, 381; *A.*, ii, 604.

[18] W. Rohn, *Z. Metallk.*, 1924, **16**, 275; *A.*, ii, 617.

[19] W. Wardlaw, F. H. Nicholls, and N. D. Sylvester, *J.*, 1924, **125**, 1910.

[20] A. Rosenheim and T. H. Li, *Ber.*, 1923, **56**, [*B*], 2228; *A.*, ii, 193.

[21] K. Lindner, *et alii*, *Z. anorg. Chem.*, 1923, **130**, 209; 1924, **137**, 66; **140**, 357; *A.*, ii, 192, 768, 864; compare *Ann. Report*, 1922, **19**, 57; see also O. Collenberg and K. Sandved, *Z. anorg. Chem.*, 1923, **130**, 1; *A.*, ii, 51.

[22] L. and H. H. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 51; *A.*, ii, 766.

in 27% yield by reduction of uranium dioxide with calcium in a crucible thickly lined with lime.[23]

Group VII.

The most satisfactory method for the preparation of fluorine is the electrolysis of fused potassium hydrogen fluoride,[24] and an improved generator is now described capable of yielding 4 litres of fluorine an hour for 20—30 hours. The electrolyte is regenerated by adding hydrogen fluoride and is then freed from water by electrolysis in a separate cell until fluorine is evolved. Heating of this anhydrous material in a copper retort yields pure anhydrous hydrogen fluoride : this was found to have a f. p. — 83° and the vapour-pressure curve was determined from that temperature up to 47°. Measurements of the vapour density of pure hydrogen fluoride up to the boiling point, combined with those of Thorpe and Hambly [25] for higher temperatures, indicate that the vapour is an equilibrium mixture of HF and $(HF)_6$, the heat of association being 6670 cals. per mol.[26]

Generation of hydrogen fluoride from calcium fluoride and sulphuric acid proceeds best at relatively high temperatures and with an excess of calcium fluoride. The converse conditions, and low concentration of water in the sulphuric acid, favour the formation of fluorosulphonic acid ; this is but slowly hydrolysed, even at 100°, to form hydrogen fluoride and sulphuric acid, which then attacks the residual calcium fluoride.[27]

Silicon tetrafluoride and water vapour do not react at temperatures between 30° and 125°, and the vapour evolved by hydrofluosilicic acid, if dried by sulphuric acid or other desiccating agents, cannot again be condensed. Thus it appears that hydrofluosilicic acid exists only in aqueous solution and not, under ordinary conditions, in the vapour phase and is a non-volatile acid like carbonic or sulphurous acid.[28]

It has been found that chlorine hydrate prepared in presence of excess of liquid chlorine has the composition $Cl_2,6H_2O$.[29]

Further work on the photochemical union of hydrogen and chlorine has confirmed Mellor's conclusion that the initial expansion

[23] W. Jander, *Z. anorg. Chem.*, 1924, **138**, 321; *A.*, ii, 767.
[24] *Ann. Report*, 1919, **16**, 49.
[25] *J.*, 1889, **55**, 163.
[26] J. Simons, *J. Amer. Chem. Soc.*, 1924, **46**, 2175, 2179; J. Simons and J. H. Hildebrand, *ibid.*, p. 2183; *A.*, ii, 847, 848.
[27] W. Traube and W. Lange, *Ber.*, 1924, **57**, [*B*], 1038; *A.*, ii, 609.
[28] C. A. Jacobson, *J. Physical Chem.*, 1923, **27**, 761; 1924, **28**, 506; *A.*, ii, 105, 782.
[29] A. Bouzat and L. Azinières, *Compt. rend.*, 1923, **177**, 1444; *A.*, ii, 103.

(the Draper effect) is a purely thermal effect of the initial combination. Observation of the effects of illumination by successive sparks (fully described in the original but difficult to summarise) leads to the conclusion that the union of hydrogen and chlorine is for the most part a purely chemical process, although the first impulse is given by the light.[30]

Reaction between gaseous ammonia and solid potassium chlorate is very vigorous and may become dangerous with high concentrations of ammonia. Investigation of the reaction, controlled by diluting the chlorate with inert material and the ammonia with air, leads to the view that it occurs according to the scheme : $KClO_3 + 2NH_3 \longrightarrow KCl + 2N + 3H_2O$; $KClO_3 + N \longrightarrow KNO_3 + Cl$; the incidence of reaction being attributed to the formation of intermediate additive compounds by direct union between potassium chlorate and ammonia, both of which are relatively unsaturated.[31]

At the ordinary temperature and in moderate concentrations of sulphuric acid, potassium permanganate oxidises iodic acid, hydriodic acid, iodine cyanide, or iodine monochloride to periodic acid; in the last case, the oxidation is incomplete, as chloride ion hinders and may even inhibit the oxidation. The oxidation of iodic acid is quantitative, and if the excess of permanganate is destroyed by adding a nitrite, and the nitrite in turn is removed by adding excess of urea, the periodic acid formed may be estimated by reduction with hydriodic acid and titration of the liberated iodine.[32]

Small amounts of pure metallic manganese may be obtained by electrolysing with a rotating cathode an electrolyte containing 30% $MnSO_4,4H_2O$, 10% $(NH_4)_2SO_4$, and 0·25% H_2SO_4, and stable, semi-solid manganese amalgams are formed by electrolysis of the same electrolyte with a well-stirred mercury cathode. If the electrolyte contains the appropriate metallic sulphate, low-manganese alloys with iron or nickel may similarly be obtained.[33]

A search for the missing element No. 43, "eka-manganese," by examination of the *X*-ray spectra of a number of manganese minerals has been unsuccessful.[34]

[30] F. Weigert and K. Kellermann, *Z. physikal. Chem.*, 1923, **107**, 1; *A.*, ii, 8.

[31] K. A. Hofmann and W. Linnmann, *Ber.*, 1924, **57**, [*B*], 818; *A.*, ii, 477.

[32] R. Lang, *Z. anorg. Chem.*, 1923, **130**, 141; *A.*, ii, 166.

[33] A. J. Allmand and A. N. Campbell, *Trans. Faraday Soc.*, 1924, **19**, 559; A. N. Campbell, *J.*, 1924, **125**, 1713; *A.*, ii, 555, 764.

[34] C. H. Bosanquet and T. C. Keeley, *Phil. Mag.*, 1924, [vi], **48**, 145; *A.*, ii, 651.

Group VIII.

A thorough study has been made of the desulphurisation of iron pyrites.[35] In dry air, it is practically complete at 800—900°; in air saturated with water vapour, the rate of removal of sulphur is greater below and less above 650° than the rate in dry air. In steam, removal of sulphur begins at 380° and the rate increases rapidly to 500° and more slowly then to 680°, at which temperature the solid phase is ferrous sulphide : on further heating, the ferrous sulphide is oxidised to triferric tetroxide with evolution of hydrogen and hydrogen sulphide. The action of carbon monoxide generally resembles that of steam. Carbon dioxide has no oxidising action on pyrites below 900°, but in this inert atmosphere dissociation of the mineral into ferrous sulphide and sulphur begins at 580° and is complete at 670°. This is in good agreement with the observation that the dissociation of pyrites in a vacuum begins at 500°, proceeds rapidly at 550°, and is complete at 670—680°.[36] From observations [35] of the partial pressure of sulphur dioxide and sulphur trioxide, it is inferred that the oxidation of pyrites occurs through the intermediate formation and decomposition of a persulphate at low temperatures and of ferrous sulphate at temperatures above about 430°.

The volume of hydrogen absorbed by an ethereal nickel sol corresponds with the formation of a hydride NiH_4, whilst the black product dried in hydrogen has the formula NiH_2; the fact that this hydride when treated with alcohol at once evolves hydrogen is regarded as additional evidence that the process of catalytic reduction in presence of nickel is essentially chemical and is due to the intermediate formation of nickel hydride.[37]

A new method has been devised for the preparation of certain double fluorides of potassium with metals of the platinum group. Finely-divided platinum or iridium is heated with the double plumbic fluoride, $3KF,HF,PbF_4$, in the latter case in a nickel crucible lined with potassium fluoride. Potassium fluoroplatinate, K_2PtF_6, forms pale yellow crystals, very slightly soluble in water (0·0023% at 25°). Potassium and lead fluoroiridiates are pink, crystalline solids, the former sparingly soluble in water but insoluble in alcohol, the latter soluble only in 10% ammonium acetate solution.[38]

Osmium tetroxide digested with concentrated hydrochloric

[35] F. C. Thompson and N. Tilling, *J. Soc. Chem. Ind.*, 1924, **43**, 37T; *A.*, ii, 341.

[36] (Mlle) G. Marchal, *Bull. Soc. chim.*, 1924, [iv], **35**, 43; *A.*, ii, 187.

[37] W. Schlenk and T. Weichselfelder, *Ber.*, 1923, **56**, [*B*], 2230; *A.*, ii, 189.

[38] H. I. Schlesinger and M. W. Tapley, *J. Amer. Chem. Soc.*, 1924, **46**, 276; *A.*, ii, 343.

acid liberates from potassium iodide exactly 4 atoms of iodine per mol. of OsO_4 and forms osmium hydroxytrichloride, $Os(OH)Cl_3$, crystallising in long, brown needles containing water and yielding with alkali chlorides hydroxypentachloro-osmates of the type $M^I_2[OsCl_5{\cdot}OH]$. The hydroxytrichloride on hydrolysis forms the black insoluble $OsO_2,2H_2O$, which is reoxidised to the tetroxide by potassium permanganate, absorbing 4 atoms of oxygen per mol. These facts are held to confirm the octavalency of osmium.[39]

Certain complex sulpho-acids of platinum, a new series of acido-amidotetrammineplatinic salts of the type $[Pt(NH_3)_4NH_2X]X_2$ ($X = Cl$, Br or NO_3), and certain pentammine platinic salts have been described.[40]

Ruthenium tetroxide and gaseous hydrogen chloride react to form tetrachloro-oxyruthenic acid as follows: $RuO_4 + 6HCl \longrightarrow H_2RuO_2Cl_4 + Cl_2 + 2H_2O$. This acid crystallises with 3 mols. of water in reddish-brown, hygroscopic needles; treated with concentrated hydrochloric acid, it yields a reddish-brown solution containing hexachlororuthenic acid and pentachlororuthenious acid thus: $H_2RuO_2Cl_4 + 4HCl \rightarrow H_2RuCl_6 + Cl_2 + 2H_2O$; $2H_2RuCl_6 \rightleftharpoons 2H_2RuCl_5 + Cl_2$.[41]

Measurements of dissociation pressure indicate that between 680° and 840° ruthenium trichloride dissociates directly into its elements without intermediate formation of lower chlorides,[42] but the chlorination of finely-powdered ruthenium at moderate temperatures (360°) by the action of chlorine containing carbon monoxide can be made to yield a brown powder, consisting mainly of ruthenium dichloride, which is insoluble in water and most other solvents, but dissolves in alcohol to form a blue solution resembling that produced by reduction of ruthenium trichloride.[43]

The cæsium, rubidium, and ammonium ruthenates of the types $M^I_2RuO_4$ and the monohydrates of the two former, resembling the corresponding potassium salts,[44] and three double sulphites of potassium or sodium with ruthenium have been prepared.[45]

H. V. A. Briscoe.

[39] F. Krauss and D. Wilken, *Z. anorg. Chem.*, 1924, **137**, 349; *A.*, ii, 772.

[40] L. Tschugaev and S. Krassikov, *ibid.*, 1923, **131**, 299; L. Tschugaev, *ibid.*, 1924, **137**, 1, 401; *A.*, ii, 268, 769, 770.

[41] S. Aoyama, *ibid.*, **138**, 249; *A.*, ii, 771.

[42] H. Remy and M. Köhn, *ibid.*, **137**, 365; *A.*, ii, 770.

[43] J. L. Howe, J. L. Howe, jun., and S. C. Ogburn, *J. Amer. Chem. Soc.*, 1924, **46**, 335; F. Krauss and H. Kükenthal, *Z. anorg. Chem.*, 1924, **137**, 32; *A.*, ii, 344, 770.

[44] F. Krauss and H. Kükenthal, *ibid.*, **132**, 315; F. Krauss, *ibid.*, p. 301; *A.*, ii, 196.

[45] H. Remy and C. Breimeyer, *ibid.*, **129**, 215; *A.*, ii, 54.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

In view of the large and increasing number of papers appearing from year to year, it has become impossible to include in this Report even such a reasonable selection of researches as will furnish a compendium of progress in the whole of the special branch of the subject specified by the above title.

The guidance and relief afforded by the Publication Committee are therefore welcome. It has been decided that contributors should now "aim at presenting a homogeneous, consecutive, and interesting account of only such major themes as may have reached a well-marked stage during the period since they were last under review. This period may frequently be several years." An endeavour has been made to fulfil this obligation in the following account, which consequently deals with fewer topics than the Reports of past years.

Optical Activity.

On comparing the specific inductive capacities of compounds of the type RX, for long wave-lengths and at normal temperatures, it is found that the substituent group X exerts a graded influence represented by the order :

$$\overset{-}{O}H \quad Cl \quad Br \quad I \quad Et \quad \overset{-}{M}e \quad \overset{+}{H} \quad CO{\cdot}OH \quad CHO \quad CO{\cdot}CH_3 \quad CN \quad \overset{+}{N}O_2,$$

that is, the values of the specific inductive capacities vary in accordance with the gradual transition of X from a highly negative to a highly positive polarity. This also roughly corresponds with the order indicating the relative polarity of the groups as deduced from the data of benzene substitution. The dissociation constants of substituted acids, in which one or other of the above series of substituents represents the group X, show a similar sequence or transition. It is now demonstrated that, in general, the replacement of a hydrogen atom in an optically active compound by a positive substituent displaces the rotation in the opposite sense to that due to a negative substituent, and that the magnitude of the displacement corresponds more or less closely to the position of the substituent in the above polar series.

It is clear that discrepancies arise where isolated values of rota-

tion taken in a limited range of solvents only are available, and where other data depend on conditions unfavourable for a true comparison.

Evidence drawn from the electromagnetic rotation of benzene and its substitution products reveals a similar sequence in the degree of polarity of positive and negative substituents.

On these considerations a hypothesis of fundamental importance has been founded.[1] It is pointed out that the rotation of an optically active compound is probably related to the electrostatic moment of the groups attached to the asymmetric carbon atom, and many of the determinations of specific rotation, confined to a single series containing variable substituents, fully bear out this view. The new hypothesis appears nearer to the truth than the conception of P. F. Frankland postulating a mechanical moment, and known as the "lever-arm-theory," and is, moreover, capable of great development. Where the substituent groups attached to an asymmetric centre contain double linkings or chromophoric groups, the problem is presented as to how far, if at all, the asymmetric centre may respond to the special characteristic of such substituents, such as polar activation, or absorption frequencies. It is concluded [2] that, instead of the adoption by such centres of these characteristics, the specialised types of substituents themselves exhibit induced asymmetry, and probably contribute directly to the rotatory power of the molecule.

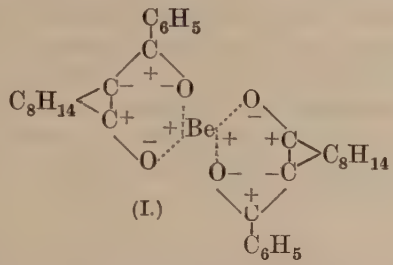
A new chapter in the study of the phenomenon of mutarotation is opened out by the discovery [3] that beryllium benzoylcamphor undergoes reversible isomeric change. The mutarotation is especially pronounced in chloroform, but has been observed also in benzene, acetone, alcohol, heptane, and *cyclo*hexane. The rate of the change is greatly accelerated by traces of piperidine or benzoic acid. The beryllium benzoylcamphor combines additively with chloroform, separating from a solution in glassy prisms containing two molecular proportions of chloroform which are gradually eliminated on keeping. It has already been established by *X*-ray analysis that in beryllium acetate each beryllium atom in the co-ordinated complex is surrounded by four oxygen atoms situated at the corners of a tetrahedron of which the metallic atom occupies the centre. On assigning a similar configuration to beryllium benzoylcamphor, it is seen that the benzoylcamphor radical is unsymmetrical and two stereoisomeric co-ordination compounds are possible, and in

[1] H. G. Rule, *J.*, 1924, **125**, 1121; H. G. Rule and T. R. Paterson, *ibid.*, p. 2155.

[2] T. M. Lowry and E. E. Walker, *Nature*, 1924, **113**, 565; *A.*, ii, 373.

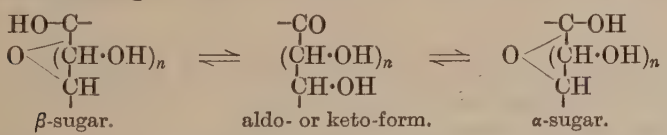
[3] H. Burgess and T. M. Lowry, *J.*, 1924, **125**, 2081.

both these forms the beryllium atom is asymmetric. The dynamic isomerism of the compound is analogous to that of α- and β-glucose and, since the mutarotation change must proceed through a third or intermediate form, it is suggested that the ring system of the co-ordination complex (I) opens out to produce a form in which the beryllium atom momentarily loses its optical activity as does the reducing group of a hexose :



(I.)

The conception that the mutarotation of sugars is dependent on the intermediate formation of a hydrate has been adversely criticised, and the simpler view that the aldose or ketose itself displays dynamic isomerism is supported by a dynamical investigation and by a series of crucial experiments.[4] The oximes, anilides, and hydrazones of sugars all show mutarotation, and the hypothesis of the formation of an aldose hydrate which functions as an intermediate product can obviously not apply to these cases.[5] The mechanism of mutarotation is best expressed by regarding it as a simple tautomeric change :



β-sugar. aldo- or keto-form. α-sugar.

Considerations based on the hypothesis of additive optical superposition lead to unexpected results in regard to the stereochemical form of several aceto-halogen derivatives of sugars. Although acetobromoglucose is transformed into β-methylglucoside by its reaction with methyl alcohol followed by deacetylation, yet the halogen derivative is now, apparently, to be regarded as an α-compound.[6]

An interesting study of catalytic racemisation is afforded by an investigation on the *l*-menthyl phenylhalogenoacetates.[7] When

[4] J. W. Baker, C. K. Ingold, and J. F. Thorpe, *J.*, 1924, **125**, 268.

[5] R. Gilmour, *ibid.*, p. 705.

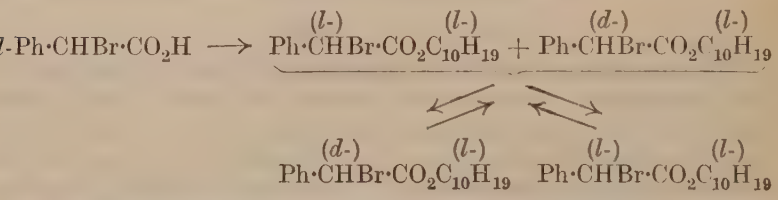
[6] C. S. Hudson, *J. Amer. Chem. Soc.*, 1924, **46**, 462, 477; *A.*, i, 371, 372; C. S. Hudson and K. P. Monroe, *ibid.*, p. 979; *A.*, i, 617.

[7] A. McKenzie and (Miss) I. A. Smith, *J.*, 1924, **125**, 1582.

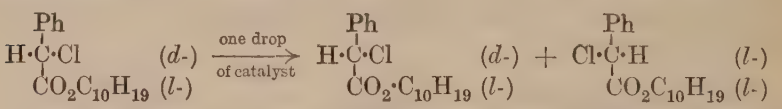
l-phenylbromoacetic acid was esterified with *l*-menthol and hydrogen chloride, the resulting crystalline ester did not consist of the ester of the *l*-acid but of the *d*-acid. Catalytic racemisation had obviously occurred during the esterification, the *l*-menthyl *l*-phenylbromoacetate being converted into a mixture of the diastereoisomerides, crystallisation of which led to the isolation of the *d*-isomeride.

The reversibility of this phenomenon is indicated by conducting a similar experiment with the latter isomeride. Digestion with alcoholic hydrogen chloride led to the isolation of a mixed ester in which the *l*-acid was in a preponderance over the *d*-acid and from this mixture the homogeneous *l*-ester was separated.

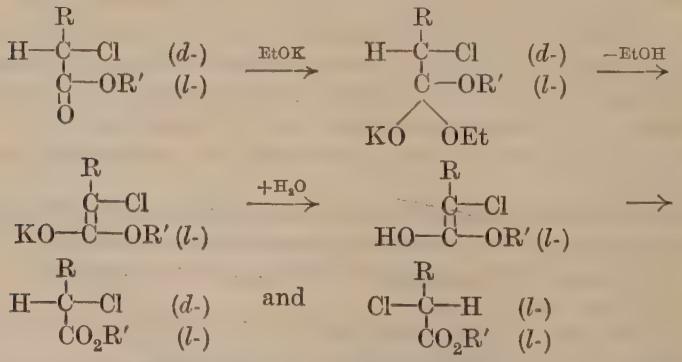
This series of striking interconversions of enantiomorphous varieties is summarised by the following scheme :—



By the agency of a single drop of potassium ethoxide it is shown to be possible to effect the following changes with the corresponding chloro-ester :



The mechanism of the interconversion is probably indicated by the scheme formulated below, except that a preponderance of the lævo-ester is formed in the final stage :



This result is not in the orthodox sense an asymmetric synthesis,

but is an example of the influence of an optically active group in directing, asymmetrically, a reversible isomeric change.

A constant product of the action of yeast on sucrose solutions is *l*-malic acid,[8] and the formation of this compound is promoted by the addition of sodium hydrogen carbonate or sodium fumarate. The resolution of *r*-malic acid has been achieved by the use of cinchonine [9] and also by the application of ammonium molybdate. The *r*-ammonium molybdomalate is not deposited from solution as such, but separates first as the lævo- and then as the dextro-isomeride.[10] From a mixture of the *d*- and *l*-salts the optical enantiomorphs can also be separated mechanically. Since the specific rotation is of the order $\pm 220°$, the purity of the fractions can readily be determined and the conversion of the salts to the free *d*- and *l*-malic acids is a simple procedure. It is observed that the *d*-malic acid, obtained through chlorosuccinic acid by the Walden inversion, contains 25% of the *l*-acid.

There is no doubt as to the existence of definite compounds such as the dimolybdomalates, $2MoO_3,C_4H_6O_5,2NH_3$, and the molybdodimalates, $MoO_3,2C_4H_6O_5,2NaOH$; and the rotatory and dispersive powers of several such salts have been determined.[11]

Uranyl malate and uranyl tartrate are found to be, not neutral salts, but complex acid salts of which disodium derivatives can be formed.[12] The unexpectedly complex nature of such salts is matched by the existence of complex antimonyl potassium tartrates, which appear to be formed when the antimonyl trioxide precipitated from potassium antimonyl tartrate redissolves in the excess of alkali added.

When a crystal of tartaric acid is cut normally to its optic axis, the section exhibits a rotatory dispersion of 2·14 as between the indigo and yellow rays, whereas for the tartrates the ratio is not more than 1·8. The higher value is almost identical with that observed for the dispersion of tartaric acid in solution. The conclusion is drawn [13] that the anomalous rotatory dispersion of tartaric acid is to be attributed to the existence of two isodynamic α- and β-forms in equilibrium, the one being dextro- and the other

[8] H. D. Dakin, *J. Biol. Chem.*, 1924, **61**, 139; *A.*, i, 1142.

[9] *Idem*, *ibid.*, 1924, **59**, 7; *A.*, i, 610.

[10] E. Darmois and J. Perin, *Bull. Soc. chim.*, 1924, [iv], **35**, 353; *A.*, i, 610; compare *A.*, 1923, i, 299; *idem*, *Compt. rend.*, 1923, **176**, 391; *A.*, 1923, i, 300.

[11] E. Darmois, *J. Phys. Radium*, 1923, **4**, 49; *Compt. rend.*, 1923, **176**, 1140; *A.*, 1923, i, 299, 535.

[12] *Idem*, *Compt. rend.*, 1923, **177**, 49; *A.*, 1923, i, 751.

[13] L. Longchambon, *ibid.*, 1924, **178**, 951; *A.*, ii, 373; T. M. Lowry and P. C. Austin, *ibid.*, p. 1902; *A.*, i, 940.

lævo-rotatory, and since the dispersion 2·14 corresponds with a specific rotation of — 70° this may be regarded as the rotatory power of the lævorotatory component. The latter is thus neither an anhydride nor an internal ether, but ordinary tartaric acid as it exists in the crystals. New work on the *X*-ray analysis of the crystal structure has led to the suggestion that the above hypothesis of the existence of dynamic isomerides is unnecessary, and that the dextrorotatory component alone exists, partly, however, in an associated or polymerised state, consisting of strings of molecules joined at the hydrogen junctions of the hydroxyl groups,[14] the structure of the crystal being in part maintained. Combating this view is the evidence from the study of changes in molecular weight and rotatory power of ethyl tartrate in formamide, benzene, and other solvents, the ester being chosen because it behaves throughout as a higher homologue of amorphous tartaric acid. In formamide, the ester is unimolecular, and the dispersion curves are complex in character.[15] In benzene, the molecular weight doubles its value at a concentration of 20%, but the rotatory power increases up to 10% and then decreases. Polymerisation is, in fact, accompanied by an exaltation of rotation, whereas the crystallographic theory demands the opposite result if the lævorotatory component of tartaric acid is a polymeride. The absence of any parallelism between the changes in rotation and molecular weight seems to dispose of the theory based on *X*-ray analysis.

A hydrated, active tartaric acid [16] is obtained by crystallising aqueous solutions below 5°, but the crystals are only stable below 10°. Methylene tartaric acid and dimethylene tartrate have been prepared,[17] and their rotatory dispersion can be expressed in one term of Drude's equation. This is also true for *d-sec*-octyl alcohol, but its oxalate exhibits a complex dispersion which cannot be expressed by the one-term equation or by Biot's law.[18] The value of the specific rotation of *d-sec*-octyl *i*-tartrate is in disagreement with the hypothesis of optical superposition.[19]

It has previously been recorded that the form of the curve obtained when $1/\alpha$ is plotted against λ^2 (α = rotatory power at wavelength λ) is linear in the case of the simpler alcohols and ethers, whilst a hyperbolic curve is obtained for most esters. In the former case, the dispersions were expressed by the one-term equation, and in the latter by the two-term Drude equation, and these classi-

[14] W. T. Astbury, *Proc. Roy. Soc.*, 1923, [*A*], **102**, 506; *A.*, 1923, i, 178.
[15] T. M. Lowry and J. O. Cutter, *J.*, 1924, **125**, 1465.
[16] M. Amadori, *Atti R. Accad. Lincei*, 1924, [v], **33**, i, 507; *A.*, i, 1163.
[17] P. C. Austin and V. A. Carpenter, *J.*, 1924, **125**, 1939.
[18] T. M. Lowry and E. M. Richards, *ibid.*, p. 1593.
[19] T. S. Patterson and C. Buchanan, *ibid.*, p. 1475.

fications have been designated as "simple" and "complex" dispersion and were held to represent cases of both optical and chemical homogeneity on the one hand and heterogeneity on the other. A homologous series of *n*-alkyl ethers of *d*-γ-nonanol, ranging from methyl to *n*-nonyl, has now been prepared, and their densities and rotations have been determined.[20] Their rotatory dispersions, with the exception of that of the methyl ether, cannot be represented by the one-term Drude equation, and cases of optical heterogeneity appear to occur, unaccompanied, however, by chemical heterogeneity. The curve obtained by plotting rotations against the number of carbon atoms of the alkyl group in the series appears smooth, except for depressions at the *n*-propyl and the *n*-octyl members, where the spiral of five additional atoms may be said to return on the α-carbon atom of the active alcohol.

In most of the earlier work, complex rotatory dispersion was always correlated with the presence of a carboxyl or ester group in which dynamic isomerism may occur, but in the results recorded above it is evident that complex dispersion is not restricted to compounds containing such groups. It is difficult to conceive of intramolecular changes taking place in so simple a grouping as that of an ether, and it becomes evident that an explanation of these results must be looked for elsewhere.

Dissatisfaction with this new system of classification has been strongly expressed, and one author [21] prefers a return to the older system of distinguishing between normal and anomalous dispersion. It is urged that the evidence for the application of the one-term Drude equation is insufficient, and that any chemical significance in the two-term equation probably lies in the similarity or otherwise of the signs. The "complex" rotatory dispersion associated with the carboxyl group or its equivalent is held to be due to the presence of one singly- and one doubly-linked oxygen atom unsymmetrically disposed in each group.

The study of the configuration of the series of amino-acids has been actively continued on the lines of Clough, and it is established that *d*-alanine belongs to the same series as *l*-lactic acid.[22] The reaction of nitrous acid with alanine, serine, and aspartic acid occurs without any Walden inversion, and these compounds, along with cystine, all have the same configuration. It is suggested that all naturally occurring amino-acids belong to the same stereochemical series.[23] β-Phthalimino-β-phenylpropionic acid has been resolved

[20] J. Kenyon and T. W. Barnes, *J.*, 1924, **125**, 1395.

[21] H. Hunter, *ibid.*, p. 1198, 1389.

[22] K. Freudenberg and F. Rhino, *Ber.*, 1924, **57**, [*B*], 1547; *A.*, i, 1173; compare *A.*, 1923, i, 215.

[23] P. Karrer, *Helv. Chim. Acta*, 1923, **6**, 957; *A.*, i, 151.

with cinchonine and the pure *d*-acid obtained.[24] The same active acid was obtained by the resolution of *r*-β-amino-β-phenylpropionic acid followed by heating the *d*-acid with phthalic anhydride. This acid, although lævorotatory in ethyl acetate, belongs to the *d*-series, accepting β-phenylpropionic acid as the reference compound.

It is announced that the possibility of the asymmetry of aliphatic diazo-compounds has been confirmed. Crude diazosuccinic ester was converted into bromosuccinic acid by hydrogen bromide[25] and hydrolysis with hydrochloric acid. Fractional crystallisation gave a product which appeared to be fairly pure *d*-bromosuccinic acid having $[\alpha]_D$ + 60·4°. Since, however, the original crude diazo-compound was prepared from *l*-asparagine, it seems not unlikely that it was contaminated at its source with malic acid, which may account for the whole of the facts.

A method of resolving some racemic alcohols into their optically active components is reported, depending on the formation of a double compound of the alcohol with digitonin.[26] Separation occurs on recrystallisation, and the active alcohol is isolated by distillation in a vacuum or in steam.

A further stereochemical study of the alkyl piperazines has resulted in the isolation of the first optically active representatives of this type of compound.[27] The *d*- and *l*-1 : 4-diphenyl-2-methylpiperazines have been separated by means of *d*-camphor-β-sulphonic acid.

Alcohols and their Derivatives.

A series of new experiments on the catalytic hydrogenation of aldehydes in presence of nickel salts has been instituted with the object of elucidating the constitution and mode of formation of the unexpected products obtained by previous workers who have utilised this and other methods of catalytic reduction. It is found[28] that ketones are converted smoothly into the corresponding secondary alcohols, and aromatic aldehydes into the primary alcohols. When aliphatic aldehydes are employed, however, the product contains not only the expected primary alcohol, but also the secondary alcohols which arise from the doubling of the carbon chain. The formation of these secondary products is ascribed to the condensation

[24] A. McKenzie and T. M. A. Tudhope, *J.*, 1924, **125**, 923; compare *ibid.*, 1921, **119**, 69.

[25] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, 1922, **54**, 101; 1923, **55**, 795; *A.*, 1923, i, 25, 663.

[26] A. Windaus, F. Klänhardt, and R. Weinhold, *Z. physiol. Chem.*, 1923, **126**, 308; *A.*, 1923, i, 586.

[27] F. B. Kipping and W. J. Pope, *J.*, 1924, **125**, 2396.

[28] Julius von Braun and Gerd Kochendörfer, *Ber.*, 1923, **56**, [*B*], 2172; *A.*, 1923, i, 1197.

of the true aldehyde with its enolised form to give an unsaturated ketone :

$$CHR{:}CH{\cdot}OH + H{\cdot}CO{\cdot}CH_2R \longrightarrow CHR{:}CH{\cdot}CO{\cdot}CH_2R + H_2O.$$

This reaction is followed by the reduction of the ketone to a secondary alcohol. An example of this kind may be illustrated by the formation from heptaldehyde of heptyl alcohol and hexylheptylcarbinol, $C_6H_{13}{\cdot}CH(OH){\cdot}C_7H_{15}$. A number of alcohols have also been prepared by catalytic hydrogenation of aldehydes in presence of activated magnesium.[29]

In presence of a suitable catalyst, such as iron covered with potassium carbonate, carbon monoxide undergoes reduction with hydrogen at 400—450°, under 150 atmospheres, to a mixture of alcohols, ketones, aldehydes, and other products. Using water gas as the initial material, this reaction proceeds with the formation of this mixture of products, which has been designated as "synthol," and it has been applied for the purpose of manufacturing motor fuel. A theoretical consideration of this process [30] reveals the various stages of the change represented by the conversion of carbon monoxide into formaldehyde, which, in the absence of bases, passes into methane. But in presence of the potassium carbonate used with the catalyst, the formaldehyde is reduced to methyl alcohol, which is converted either directly or through methyl formate into acetic acid, the stepwise reduction of which gives acetaldehyde and ethyl alcohol, whilst its catalytic decomposition gives acetone. A repetition of these operations yields the analogous members of the three-carbon series, and so the process continues to the stage represented by a chain of seven or eight carbon atoms. At this stage, the synthetic changes cease owing to the instability of the higher products under the experimental conditions employed.

The conditions governing the "alcoholic fermentation" of formaldehyde by osmium have been submitted to careful investigation.[31] It is found that osmium catalyses the reduction of formaldehyde to methyl alcohol only when the metal is present in the colloidal or highly dispersed condition. This condition is attained by adding to the formaldehyde a compound such as osmic acid, which is then reduced to a highly active form of the metal.

A new method for the reduction of esters is described which leads to almost theoretical yields of aliphatic alcohols.[32] An ethereal

[29] Badische Anilin- und Soda-Fabrik, D.R.-P. 384351; from *Chem. Zentr.*, 1924, i, 2398; *A.*, i, 1189.

[30] E. Fischer and H. Tropsch, *Ber.*, 1923, **56**, [*B*], 2428; *A.*, i, 131.

[31] E. Müller, *Z. physikal. Chem.*, 1923, **107**, 347; *A.*, 1924, i, 833; compare *A.*, 1922, i, 110.

[32] H. J. Prins, *Rec. trav. chim.*, 1923, **42**, 1050; *A.*, 1923, i, 1172.

solution of the ester is used, to which is added a solution of sodium acetate to form a separate lower layer. At — 5°, sodium and 80% acetic acid are admitted in sufficient amounts to maintain the ethereal solution slightly acid. Quantities of 0·5 kg. of ester require 3 to 5 days for the completion of the reaction, and an excess of approximately 30% of sodium is employed.

Phase-rule considerations have been successfully applied to the problem of the manufacture of ether, and it is shown that the system H_2SO_4–EtOH–H_2O–Et_2O–$EtHSO_4$ has three degrees of freedom. The state of equilibrium, with particular reference to ether,[33] is practically independent both of temperature and of sulphuric acid concentration. A thermodynamic study of the conditions of the reaction enables results to be deduced which agree with experimental and working experience. Using the Williamson method for the preparation of pure ethyl ether, a yield of 80% may be obtained [34] by condensing ethyl iodide with sodium ethoxide.

The view that ethers are stable compounds, unacted upon by sodium, is confuted by a comprehensive study which has been instituted with the object of determining the relative tenacity with which different radicals are linked to the oxygen atom.[35] Diethyl ether is decomposed by sodium at 200—240° into ethylene, ethyl alcohol, and probably also to ethane and hydrogen. The increasing order of tenacity towards oxygen is represented by the series benzyl, ethyl, *iso*amyl, β-naphthyl, α-naphthyl, and phenyl. Exposure of ethyl ether to the air is known to confer oxidising properties on the substance, and three examples of ether peroxide formation have been noticed,[36] and the products isolated and analysed. These are represented by propyl, *n*-butyl, and methylenediethyl ethers. In other cases, owing to the higher boiling points of the ethers, isolation was not possible, and aldehydes, esters, acids, and hydrogen peroxide were formed.

When the glycols, mixed with acetone, are heated in the presence of sulphuric acid, their acetone compounds or *iso*propylidene ethers are readily prepared. Examples are given of this reaction as conducted with ethylene glycol, propane-αβ-diol, propane-αγ-diol, glycerol, and its monochlorohydrin. Exact physical data are recorded [37] for these and other analogous compounds, and the equilibrium constants of the reaction, acetone + diol $\rightleftharpoons$ *iso*propyl-

[33] J. Desmaroux, *Mém. Poudres*, 1923, **20**, 335; *A.*, i, 484.

[34] W. B. S. Bishop, *J. Soc. Chem. Ind.*, 1924, **43**, 23T; *A.*, i, 363.

[35] P. Schorigin, *Ber.*, 1924, **57**, [*B*], 1627; *A.*, i, 1185; compare *A.*, 1923, i, 207.

[36] A. M. Clover, *J. Amer. Chem. Soc.*, 1924, **46**, 419; *A.*, i, 363.

[37] J. Böeseken and P. H. Hermans, *Rec. trav. chim.*, 1923, **42**, 1104; *A.*, i ,257.

idene ether + water, have been ascertained. It is shown that the glycols combine with the same facility with acetone as they do with boric acid.

Crystalline ethylglycerol triformin is readily prepared from ethyl glycerol and 96% formic acid, whilst the mono-, di-, and tri-formins are obtained by using the industrial 88% formic acid.[38] By distilling the mixture of the mono- and di-formins, β-ethylallyl formate and the formin of vinylethylcarbinol were isolated. The paper contains a discussion of the mechanism of the reactions involved in the synthesis of these alcohols and their formins from the three isomeric mono- and di-formins.

Other new derivatives of the glycol series are represented by the synthesis of dicarbomethoxy glycol and the corresponding dicarbethoxy-compound. Of noteworthy interest are the substances of similar type prepared by the condensation of glycerol with chloroformic esters.[39] Either two or three of the hydroxyl groups in glycerol may be protected by the introduction of the group –CO·OR, and a compound of the true carbonate type is represented by monocarbomethoxy glycerol carbonate, $CO_2Me{\cdot}O{\cdot}CH_2{\cdot}\overset{CH_2{\cdot}O}{\overset{|}{C}}H{-}O\rangle CO$. A similar substitution product is obtained from ethyl tartrate.

Oxidation of the acetyl ester of oleic alcohol with permanganate yielded both nonoic and acetylhydroxynonoic acids. Since this ester also gives, on reduction, the acetyl derivative of normal octadecyl alcohol, the formula $CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH[CH_2]_7{\cdot}CH_2{\cdot}OH$ is established [40] for oleic alcohol and the alcohol is identical with that obtained from ethyl oleate. A comparison of the physical constants of the alcohol with those of elaidic alcohol is given; the stereoisomerides may be sharply differentiated by their melting points, and show no tendency to undergo interconversion.

A simple and convenient process for the laboratory preparation of ethyl sulphate is reported.[41] A mixture of alcohol and concentrated sulphuric acid is allowed to flow through a capillary tube into a heated vacuum flask containing anhydrous sodium sulphate. At 155—165°/20—45 mm., distillation of ethyl sulphate takes place, and a pure product is obtained by washing. Methyl ethyl sulphate is prepared [42] by adding ethyl chlorosulphonate to a suspen-

[38] R. Delaby, *Ann. Chim.*, 1923, [ix], **20**, 196; *A.*, 1923, i, 1171; compare *ibid.*, p. 993.

[39] C. F. Allpress and W. Maw, *J.*, 1924, **125**, 2259.

[40] Y. Toyama, *Chem. Umschau*, 1924, **31**, 13; *A.*, i, 257; compare *A.*, 1922, i, 895.

[41] E. V. Lynn and H. A. Shoemaker, *J. Amer. Chem. Soc.*, 1924, **46**, 999; *A.*, i, 605.

[42] T. K. Thayer, *ibid.*, p. 1044; *A.*, i, 604.

sion of sodium methoxide in dry ether. Using methyl ethyl sulphate as an alkylating agent, a yield of 56·7% of anisole was isolated from phenol and also 13·4% of phenetole, as compared with the formation of 74·2% of anisole by the use of methyl sulphate. By a method [43] of preparation analogous to that described above, propyl, *iso*propyl, *n*-butyl, and *iso*amyl ethyl sulphates have been obtained. Magnesium phenyl bromide reacts with these ethereal salts, yielding ethylbenzene.

Carbohydrates.

Photosynthesis.

The problem of the mechanism of assimilation of carbon dioxide by the plant and its utilisation in carbohydrate synthesis is of fundamental importance, but we are undoubtedly far from achieving any immediate solution. Little more than tentative theories can for the moment be advanced, and it is unfortunate that these hypotheses are sometimes unaccompanied by experimental evidence, or are based on the slenderest of premises. The claim to have established the photochemical synthesis of sugars from formaldehyde was made two years ago and rested largely on qualitative or empirical tests. Until recently,[44] no analysis of this product was available, but it now appears that more than 80% of the material obtained by this procedure consists of non-sugar compounds which contain hydroxyl groups.[45] Only a portion, which, on a favourable estimate, could not exceed 9—10% of the total, had properties which resembled those of a hexose and no identification with known *dl*-hexoses was attempted. Ketoses and polysaccharides of the hexose type were absent. In view of these facts, and considering also that ordinary solutions of commercial formaldehyde contain many impurities, one feels that chemists may wish to be reassured that contact with traces of well-known polymerising agents may not have been primarily responsible for the small proportion of hexoses which were apparently recognised. The most recent experimental method renders this attitude of caution still more necessary, since the use of calcium or magnesium carbonate is introduced into the process. It does not appear what is the effect, on these mineral carbonates, of light of the wave-lengths employed, but it is not inconceivable that traces of potassium carbonate may have been formed by double decomposition with potassium salts in the solution. It has been shown by Loew that 0·1% of potassium carbonate is effective in polymerising formaldehyde to a sugar.

[43] L. Bert, *Compt. rend.*, 1924, **178**, 1182; *A.*, i, 605.
[44] E. C. C. Baly, *J. Ind. Eng. Chem.*, 1924, **16**, 1016, 1085.
[45] J. C. Irvine and G. V. Francis, *ibid.*, p. 1019; *A.*, i, 1826.

A claim has been made to the synthesis of formaldehyde, utilising a process in which basic lead carbonate is distilled with hydrogen peroxide,[46] and, on the basis of this experiment, the author puts forward a hypothesis for the assimilation of carbon dioxide, according to which sunlight decomposes water with the formation of hydrogen and hydrogen peroxide : $2H_2O \longrightarrow H_2O_2 + H_2$. The carbon dioxide is then said to react with the hydrogen peroxide and hydrogen to give formaldehyde, oxygen, and water. The initial reaction on which this theory is based has been confirmed, but it is also shown that the reduction of carbon dioxide proceeds, not from the hydrogen peroxide, but from the small amounts of organic preservatives, for example, acetanilide, which are used to stabilise the commercial reagent,[47] and thus the theory is devoid of foundation.

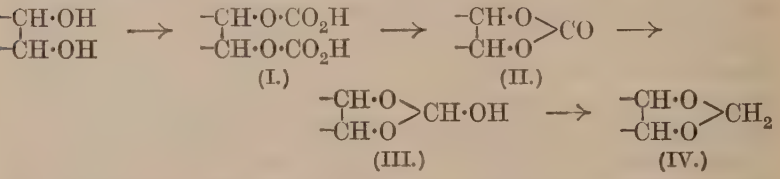
A more promising approach to the problem is indicated in the plan of examining the processes involved in carbon dioxide assimilation by a consideration of each stage separately. The first step in the photosynthesis is probably the absorption of carbon dioxide by some material of the plant. This stage may involve the additive formation of a definite series of compounds, and may be followed by a second stage in which the combined carbon dioxide, for example, an organic carbonate, undergoes reduction. Whether this stage is immediately succeeded by the appearance of formaldehyde as such or in its "activated" or its hydrated state, is more than doubtful. The manner in which the reduced carbon dioxide is utilised in the synthesis of a carbohydrate is again to be regarded as another or third stage.

Taking the first of these stages, it is now shown that dried and powdered leaves, which are afterwards moistened, are able to absorb carbon dioxide from the atmosphere in the dark.[48] Helianthus leaves treated in this way absorbed as much as 4·59 mg. of carbon dioxide for each gram of the dried leaf. The chemical agent responsible for this absorption in the dried leaf may be partly extracted with cold alcohol, with cold water which has been saturated with ether, and, to a smaller extent, with water alone; but the extracted material does not possess a capacity for absorption equal to that of which the leaf has been deprived, except in the case of the extract from aqueous ether. The absorptive capacity of the leaf is destroyed by heat. It is considered that the leaf of the plant absorbs carbon dioxide by a mechanism resembling that by which the blood of mammals serves to free the tissues from this gas. The major

[46] T. Thunberg, *Z. physikal. Chem.*, 1923, **106**, 306; *A.*, 1923, i, 1271.
[47] A. Bach and M. Monosson, *Ber.*, 1924, **57**, [*B*], 735; *A.*, i, 612; compare *A.*, 1923, i, 1271.
[48] H. A. Spoehr and J. M. McGee, *Science*, 1924, **59**, 513; *A.*, i, 1392.

portion of the carbon dioxide may be absorbed by proteins in the leaf, leading from this primary union to asymmetric synthesis of carbohydrates in the chlorophyllous plant.

This function, ascribed to proteins, of uniting with carbon dioxide is known to be shared by chlorophyll,[49] which has similarly been regarded by Willstätter as participating in the initial mechanism. Furthermore, it has recently been shown that sugars are able to form definite carbonates, many of the synthetic derivatives of which have been isolated as crystalline compounds. The suggestion is therefore made that sugars,[50] in common with other plant products, may share in the function of combining with carbon dioxide in the leaf, giving definite additive compounds of the nature of acid or normal carbonates (I and II), the former possibly existing as salts. These primary carbonates may quickly undergo reduction and appear as an orthoformic acid derivative (III) or a formaldehyde derivative (IV), as illustrated by the scheme :—



The compounds (III) and (IV) would yield, respectively, formic acid and formaldehyde on hydrolysis. The type of dioxymethylene linking represented in (IV) occurs freely in natural products, and the reverse process of passing from the grouping (IV) to that of (II) is already understood. This tentative suggestion receives some kind of support from the circumstance that a primitive form of carbohydrate has been isolated from the cabbage leaf having the constitution (V).

This compound may represent a hydrolysis product of the dioxymethylene derivative (VI) of a hydrated glycollaldehyde, or may, as the authors suggest,[51] be a condensation product of the latter with formaldehyde.

It is unlikely that any of these theories contains the whole truth, but research along such lines should lead to some substantial progress.

[49] R. Willstätter and A. Stoll, *Ber.*, 1917, **50**, 1791; *A.*, 1918, i, 207; *ibid.*, p. 243.

[50] C. F. Allpress and W. N. Haworth, *J.*, 1924, **125**, 1223.

[51] H. W. Buston and S. B. Schryver, *Biochem. J.*, 1923, **17**, 470; *A.*, 1923, i, 1062.

A theoretical paper, in which much of the earlier experimental work on this subject is reviewed, also advances a new hypothesis,[52] according to which the primary process of assimilation is a photo-autoxidation consisting in the formation of a lipoid peroxide sparingly soluble in water. The second process is the formation of an albumin–carbon dioxide complex, and this is followed by the interaction of both these products with water, whereby oxygen is released and the carbohydrate may be reduced by hydrogen peroxide (Wislicenus), or, alternatively, an albumin–carbon peroxide is formed, through which reduction to formic acid and formaldehyde occurs. The fourth process is the recombination of oxygen with the lipoid oxide to regenerate the peroxide. This occurs in the presence of light in chlorophyll-bearing cells and the cyclic process is repeated, the lipoid peroxide functioning as a photochemical motor. Chlorophyll appears not to take a part in the assimilation process beyond that of the promotion of the photo-autoxidation of the lipoid. The controversial nature of this problem is indicated by several other papers contributing alternative theories or conclusions.[53]

Further experiments serve to confirm the modern view that sugars are the first members of the carbohydrate group to be synthesised by the plant.[54] Probably the sugar initially formed is sucrose, which is transformed into monoses and finally into starch, inulin, or cellulose.[55] The opinion that monoses are the first sugars to be produced has, however, its adherents, whilst others prefer to regard starch as an early product in the photosynthetic process. The interesting observation is made that plane-polarised light greatly accelerates the hydrolysis of starch by diastase,[56] and photomicrographs illustrating this process accompany the paper.

Monosaccharides.

The fructose penta-acetates present certain optical anomalies; the α- and β-forms of the hexa-acetates of *d*-α-mannoheptose have been prepared, and a third variety, possessing probably a different oxide-ring structure, is now reported. Fluoro- and bromo-tetra-acetylfructoses have been obtained as crystalline substances,[57] and

[52] Wo. Ostwald, *Kolloid-Z.*, 1923, **33**, 356; *A.*, i, 250.

[53] J. Peklo, *Chem. News*, 1924, **129**, 90; *A.*, i, 1018; F. Weigert, *Z. physikal. Chem.*, 1923, **106**, 313; 1924, **109**, 79; *A.*, 1923, i, 1271; 1924 i, 922; T. Sabalitschka and H. Riesenberg, *Biochem. Z.*, 1924, **144**, 545, 551; *A.*, i, 475; H. Coupin, *Compt. rend.*, 1924, **178**, 1572; *A.*, i, 808.

[54] E. C. Miller, *J. Agric. Res.*, 1924, **27**, 785; *A.*, i, 1021.

[55] T. Weevers, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 46; *A.*, i, 810.

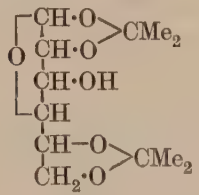
[56] E. C. C. Baly and E. E. Semmens, *Proc. Roy. Soc.*, 1924, [*B*], **97**, 250.

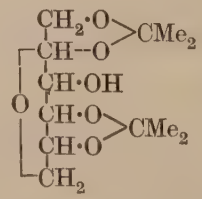
[57] D. H. Brauns, *J. Amer. Chem. Soc.*, 1923, **45**, 2381; *A.*, 1924, i, 265; C. S. Hudson, *ibid.*, 1924, **46**, 477; *A.*, i. 372; C. S. Hudson and K. P. Monroe, *ibid.*, p. 979; *A.*, i, 617.

also the fluoro-, chloro-, and iodo-triacetyl derivatives of *l*-arabinose. The differences in their specific rotations are approximately proportional to the differences in the atomic diameters of the halogen atoms present in each.[58] Striking changes are introduced in the rotatory power of sugars in presence of concentrated hydrochloric acid at low temperatures, and a paper recording these results and offering explanations for this behaviour is contributed.[59]

Much attention has recently been directed to the sugar derivatives known as the acetone compounds, which were originally described by E. Fischer. Variations in the methods of preparation are described, and several new compounds have been isolated. Differences of opinion exist as to the constitution of glucose diacetone. Levene and Meyer [60] have methylated this substance and isolated the same monomethyl glucose as that described by Irvine and Hogg,[61] who regarded it as the 6-methyl glucose. The former authors have, however, ascribed to this derivative the constitution of 3-methyl glucose, and base their contention on its ability to give a monomethyl saccharolactone on oxidation. The latter product gives rise to 3-methyl *d*-glucuronic acid on reduction and not to the *l*-form. The same conclusion as to the structure of glucose diacetone is drawn independently by other authors [62] from the study of its hydrazino-substitution derivative, and an analogous formula is allocated to fructose diacetone. This has the effect of giving glucose diacetone a butylene-oxide structure (I) and fructose diacetone an amylene-oxide structure (II), which is contrary to the view usually held.

(I.)





(II.)

The many anomalies that have been mentioned obviously require very careful reinvestigation. Fructose β-diacetone has been prepared, both from sucrose and inulin, and also from the α-diacetone.

[58] D. H. Brauns, *J. Amer. Chem. Soc.*, 1924, **46**, 1484; *A.*, i, 837.

[59] László Zechmeister, *Z. physikal. Chem.*, 1922, **103**, 316; *A.*, 1923, i, 183.

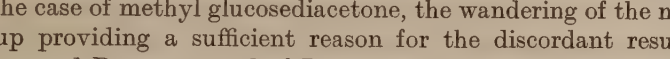
[60] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 1923, **57**, 317, 319; 1924, **60**, 173; *A.*, i, 14, 944; O. Svanberg and S. W. Bergman, *Arkiv Kemi, Min., Geol.*, 1924, **9**, 1; *A.*, i, 1285.

[61] J. C. Irvine and T. P. Hogg, *J.*, 1914, **105**, 1386.

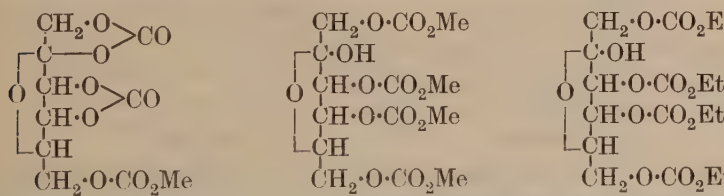
[62] K. Freudenberg and Ralph M. Hixon, *Ber.*, 1923, **56**, [*B*], 2119; *A.*, 1923, i, 1179; K. Freudenberg and Arnold Doser, *ibid.*, p. 1243; *A.*, 1923, i, 652.

The β-derivative is more resistant to hydrolysing agents than the α-compound, and for this reason the authors [63] consider that the two are structurally and not stereochemically related as supposed by Irvine and Garrett, and Irvine and Patterson.[64] A curious example of the migration of the benzoyl group in benzoylglucose monoacetone has been noticed, from which it is inferred that the benzoyl group changes from position 6 to position 3 in the glucose chain. The author [65] suggests that such an explanation might apply to the case of methyl glucosediacetone, the wandering of the methyl group providing a sufficient reason for the discordant results of Irvine and Patterson and of Levene and Meyer.

A new type of sugar compound has been synthesised [66] represented by the sugar carbonates, derivatives of which are shown to exist in two forms : (A), the normal carbonates, and (B), the acid carbonates :



The type (A) resembles the acetone derivatives in structure, but both types differ from the acetone compounds in being hydrolysed, not only by dilute acids, but also with dilute alkalis even in the cold. Their preparation is conducted by acting on the sugars with chloroformic esters in presence of (1) sodium hydroxide or (2) pyridine. Using these two methods in turn, crystalline derivatives of fructose were isolated which are represented by the following formulæ :



Crystalline derivatives of galactose and of difructose were also obtained, as well as other similar compounds from glucose, sucrose, and mannitol. These compounds are unique in character and display remarkable changes in rotation on keeping in the dark.

The isolation of α-mannose is recorded for the first time,[67] and its rotation agrees with that calculated from theoretical considerations by Hudson. Its penta-acetate has been obtained, the proper-

[63] H. Ohle and I. Koller, *Ber.*, 1924, **57**, [*B*], 1566; *A.*, i, 1168.

[64] J. C. Irvine and C. S. Garrett, *J.*, 1910, **97**, 1277; J. C. Irvine and J. Patterson, *J.*, 1922, **121**, 2146.

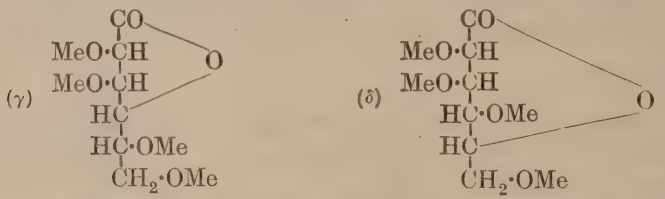
[65] H. Ohle, *Ber.*, 1924, **57**, [*B*], 403; *A.*, i, 497.

[66] C. F. Allpress and W. N. Haworth, *J.*, 1924, **125**, 1223.

[67] P. A. Levene, *J. Biol. Chem.*, 1923, **57**, 329; 1924, **59**, 129, 141; *A.*, 15, 615.

ties of which conform to those already determined from theoretica considerations. By conducting the glucoside formation of mannose under conditions identical with those observed by E. Fischer in his preparation of γ-methylglucoside, the analogous γ-methylmannoside has been isolated and converted into the trimethyl and tetramethyl derivatives.[68] From the latter, tetramethyl γ-mannose was obtained as a crystalline substance having a dextrorotation. It is suggested that during the preparation of these compounds auto-condensation was observed, giving rise to a tetramethyl di-mannose. The constitution of the above derivative, tetramethyl γ-mannose, has not been determined by oxidation, but in view of the results communicated by Levene and Meyer and described below,[69] it is probable that this sugar is a 1 : 4- or a 1 : 5-oxide.

From considerations such as those applied by J. Pryde in the case of galactonolactone, it has been found that mannose gives rise to two different tetramethyl mannonolactones according as (*a*) mannonolactone is methylated or (*b*) tetramethyl mannose of the ordinary form is oxidised to the lactone. Both products are dextrorotatory, and this is entirely in accord with Hudson's rule, although the authors themselves express some hesitation in applying their results. They are to be interpreted in the sense that both lactones have the oxide ring on the right of the chain, one of them being therefore a 1 : 4- (γ) and the other a 1 : 5-lactone (δ).



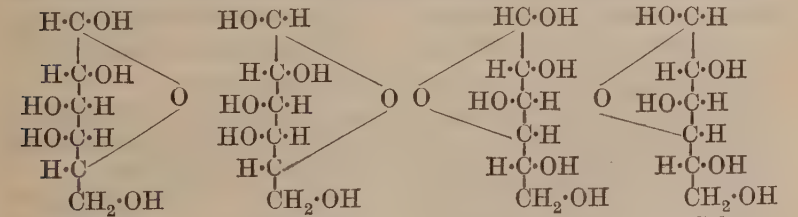
Already it has been demonstrated by J. Pryde [70] that ordinary tetramethyl galactose has an amylene-oxide structure giving a dextrorotatory lactone on oxidation, and since this variety of galactose has been isolated from lactose, melibiose, and raffinose, it is established that natural galactose occurs as a 1 : 5-oxide. A new structural form of galactose has recently been prepared [71] as γ-methyl galactoside by the action of methyl-alcoholic hydrogen chloride in the cold. It is readily transformed into a tetramethyl γ-galactose, differing from the usual variety in that the equilibrium mixture of α- and β-forms is lævorotatory, whereas the normal compound is pronouncedly dextrorotatory.

[68] J. C. Irvine and W. Burt, *J.*, 1924, **125**, 1343.
[69] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 1924, **60**, 167; *A.*, i, 944.
[70] J. Pryde, *J.*, 1923, **123**, 1808; 1924, **125**, 520.
[71] W. N. Haworth, D. A. Ruell, and G. C. Westgarth, *ibid.*, 1924, **125**, 2468.

Oxidation of the new γ-isomeride leads to a tetramethyl galactonolactone which is lævorotatory, having a 1 : 4- or butylene-oxide ring, and identical with that isolated by the methylation of the galactonolactone obtained by oxidising free galactose itself.

Having regard to the fact that Levene and Meyer have obtained a new tetramethyl mannonolactone by methylation of mannonolactone, and that the latter is considered by Hudson to be a true γ-lactone, *i.e.*, having its lactone ring in the 1 : 4-position, it would appear that the new γ-form of tetramethyl mannose isolated by Irvine and Burt should correspond to this lactone in structure, since the normal form of tetramethyl mannose gives a lactone having quite different properties. The situation thus created would mean that of the aldohexoses so far constitutionally examined with respect to their internal oxide rings, galactose and mannose exist normally as 1 : 5- or amylene-oxides. Glucose remains in doubt, although the structure uniformly ascribed to it is that of a 1 : 4- or butylene-oxide. But should glucose be drawn into the analogy with galactose and mannose, then the fortuitous terminology of a γ-sugar will acquire a new and general meaning, in that such a compound will be one that gives rise, on oxidation of its tetramethyl derivative, to a γ-lactone as understood in the ordinary sense. Such a simplification and interpretation of the nomenclature would be welcome.

As the facts now stand, *d*-galactose in common with *d*-glucose and *d*-mannose can exist as two structural varieties differing only in respect of the type of the oxide ring which they possess. Each of these structural varieties gives rise to α- and β-stereo-modifications, and, in addition, the same number of isomerides will occur for each of the three *l*-sugars. Consequently, eight modifications (four for the *d*- and four for the *l*-sugars) may be regarded as having definitely been shown to be capable of existence for each of the monosaccharides glucose, mannose, and galactose. The formulation of these in the case of *d*-galactose may be represented as follows:



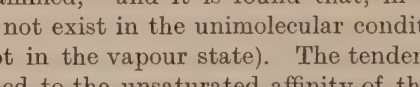
Normal *α-d*-galactose. Normal *β-d*-galactose. *γ-α-d*-Galactose. *γ-β-d*-Galactose.

It may now be regarded as established that all *d*-hexoses can exist in four such modifications and the general chemistry of the sugars should be expanded to accommodate these facts. The simple

pentoses may similarly fall into line and, should this be the case, the total number of modifications of the aldo-hexoses becomes sixty-four, and of the pentoses, thirty-two. Small wonder indeed if, considering this complexity, sugars do not respond easily to attempts at their isolation in pure stereochemical forms. Hudson's endeavours in this direction have been surprisingly successful, and such comments as may be made on minor inaccuracies in his application of the principle of optical superposition to the sugar group [72] must allow for the considerable difficulties encountered.

Studies of oxide-ring compounds, in which the oxygen bridge bears a resemblance to the structure of the sugars, continue to provide valuable information. In the past, the structure of a propylene- or of an ethylene-oxide ring was allocated to γ-sugars, but the properties of the compounds :

have been examined,[73] and it is found that, in both cases, such substances do not exist in the unimolecular condition but as polymerides (except in the vapour state). The tendency to polymerisation is ascribed to the unsaturated affinity of the bridge oxygen, and is the greater the nearer the linked carbon atoms are situated. A compound of the butylene-oxide type (II) is described,



which is a dynamic isomeride of the aldehyde (I). Both these compounds are unimolecular,[74] and it will be observed that the oxide-ring is of the butylene type. Other experiments which have been instituted should lead to further knowledge on this subject.[75]

Fischer's supposition that glycuronic acid is produced in the animal organism by the oxidation of a glucose derivative in which the reducing group is protected, receives support from an investig-

[72] T. S. Patterson and C. Buchanan, *J.*, 1924, **125**, 2579.

[73] M. Bergmann and E. Kann, *Annalen*, 1924, **438**, 278; *A.*, i, 1042; M. Bergmann and S. Ludewig, *ibid.*, 1924, **436**, 173; *A.*, i, 490; compare Bergmann and Miekeley, *A.*, 1921, i, 763; Fischer, *A.*, 1895, i, 437.

[74] Burckhardt Helferich and Hans Köster, *Ber.*, 1923, **56**, [*B*], 2088; *A.*, 1923, i, 1177.

[75] H. Hibbert and J. A. Timm, *J. Amer. Chem. Soc.*, 1923, **45**, 2433; 1924, **46**, 1283; *A.*, i, 16, 710; M. Bergmann, A. Miekeley, and F. Stather, *Ber.*, 1923, **56**, [*B*], 2255; *A.*, i, 5; H. Hibbert and R. R. Read, *J. Amer. Chem. Soc.*, 1924, **46**, 983; *A.*, i, 613; P. A. Levene, *J. Biol. Chem.*, 1924, **59**, 135; *A.*, i, 615.

ation [76] which describes the isolation of methyl glycuronide by oxidation of α-methylglucoside with sodium hypobromite, or Fenton's reagent. Glucose, in presence of barium hypobromite, is found to undergo a stepwise oxidation, in which the chief products [77] are gluconic acid, β-ketogluconic acid, and arabonic acid.

A quantitative study of the interaction of glucose and phenylhydrazine has confirmed Fischer's speculation as to the fate of the third molecule of the latter reagent during osazone formation. The equation representing the reduction of phenylhydrazine to aniline and ammonia is substantiated. In the same paper,[78] valuable practical details for the preparation of osazones in optimum yield are described.

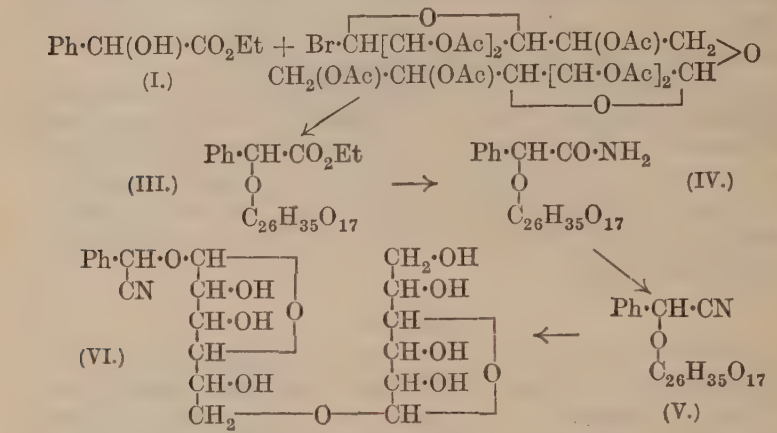
Glucosides.

The proof of the identity of the biose of amygdalin with gentiobiose was given last year; [79] this work has been repeated and confirmed by independent workers, and is supported by other evidence.[80] A calculation of the rotations of two derivatives of amygdalin, namely, *iso*amygdalin and prulaurasin, has shown [81] that the biose chain of amygdalin has the same rotation value as the chain of gentiobiose.

This preliminary structural inquiry has now been followed by the complete synthesis of amygdalin in accordance with the following scheme.[82] The condensation of (I) ethyl *dl*-mandelate with (II) β-bromohepta-acetylgentiobiose was effected in the presence of silver oxide, and gave rise to the crystalline ethyl $d + l$-hepta-acetylamygdalinate (III), a result which was communicated in an earlier paper by one of the authors. The latter ester was transformed into the amide (IV) by the action of ammonia dissolved in methyl alcohol, and this reagent simultaneously removed the acetyl groups, forming $d + l$-amygdalinamide. Acetylation of this acid amide in pyridine restored the seven acetyl residues, and recrystallisation of the product yielded two isomeric forms of hepta-acetylamygdalinamide (IV) combined with 1 mol. of pyridine. One of these stereoisomeric forms was digested with phosphoric oxide in xylene solution and underwent dehydration from the acid amide to the nitrile, hepta-acetylamygdalin (V), which was lævorotatory to the same degree as the acetylated product of natural

[76] K. Smoleński, *Roczniki Chemji*, 1923, **3**, 153; *A.*, 1924, i, 10.
[77] M. Hönig and F. Tempus, *Ber.*, 1924, **57**, [*B*], 787; *A.*, i, 712.
[78] E. Knecht and F. P. Thompson, *J.*, 1924, **125**, 222.
[79] W. N. Haworth and B. Wylam, *J.*, 1923, **123**, 3120.
[80] G. Zemplén, *Ber.*, 1924, **57**, [*B*], 698.
[81] C. S. Hudson, *J. Amer. Chem. Soc.*, 1924, **46**, 483; *A.*, i, 372.
[82] R. Campbell and W. N. Haworth, *J.*, 1924, **125**, 1337.

amygdalin and with which it was shown to be identical. Deacetylation with alcoholic ammonia gave natural amygdalin (VI).



This synthesis of amygdalin by R. Campbell and W. N. Haworth has since been repeated independently by two other workers [83] and is substantiated at each stage by their results. There remains therefore no reason for doubt that this important and historic natural glucoside is *d*-mandelonitrile-β-gentiobioside. The convention employed in referring amygdalin to the *d*-series is based on the observation that lævorotatory mandelic acid is related to *d*-malic acid. Still further confirmation of this constitution is afforded by a modification of the first synthesis of amygdalin which is described above.

The initial stage in this later synthesis by Zemplén and Kunz [84] was achieved by the interaction of silver *d*-mandelate and acetobromogentiobiose, and the by-product from this condensation was hexa-acetyl-*d*-amygdalo-lactone, which was converted by alcoholic ammonia into *d*-amygdalinamide, as compared with the corresponding $d + l$ compound isolated in the earlier synthesis. From this product synthetic amygdalin was obtained by a series of stages similar to those previously formulated.

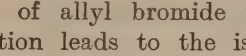
Three crystalline isomerides of tetra-acetyl *d*-methylmannoside have now been isolated.[85] One of these, prepared from β-*d*-mannose pentacetate having a lævorotation, possesses properties not generally characteristic of acetylated glucosidic derivatives of the sugars. Alkaline hydrolysis removes only three of the four acetyl radicals,

[83] R. Kuhn and H. Sobotka, *Ber.*, 1924, **57**, [*B*], 1767; *A.*, i, 1330.

[84] G. Zemplén, *Ber.*, 1924, **57**, [*B*], 698; *A.*, i, 617; G. Zemplén and A. Kunz, *ibid.*, pp. 1194, 1357; *A.*, i, 975, 1215.

[85] J. K. Dale, *J. Amer. Chem. Soc.*, 1924, **46**, 1046; *A.*, i, 615.

although all four are eliminated by acid hydrolysis. The specific rotations of these three isomerides provide a close parallel to the three crystalline tri-acetyl *l*-methylrhamnosides and one of them is probably a γ-form. Glucosidic compounds of mannose with glycol and glycerol have been prepared by the synthetic agency of α-*d*-mannosidase.[86] A yield of 40% of pure β-methylglucoside from the reaction of glucose with methyl sulphate and alkali is reported.[87] Experiments on the substitution of sugar residues for the glycerol group in olive oil have led to the production of a synthetic fat containing a methylglucoside residue.[88] This is formulated as below, where X represents the oleyl substituent



Condensation of allyl bromide with various carbohydrates in alkaline solution leads to the isolation of tetra-allyl α-methyl glucoside, penta-allyl sucrose, allyl dextrin, allyl inulin, the allyl starches, and allyl cellulose.[89] A new method is also given for the extraction from plants of the pure glucosides which are soluble in water,[90] and some novel glucosides and galactosides of thiols are described.[91]

Disaccharides.

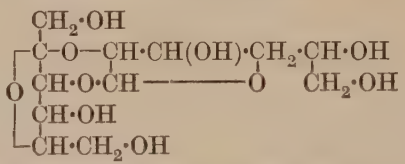
A synthesis of maltose has been effected by the action of yeast maltase at 37° on a 40% solution of dextrose. After fermentation of the residual glucose, crystalline maltose [92] was isolated from the portion of the residue soluble in alcohol, whereas the insoluble portion yielded slightly impure revertose in much smaller quantity. Croft Hill's experiments, it will be recalled, yielded chiefly revertose.

Despite numerous attempts which have been made to achieve the synthesis of sucrose, this biose successfully frustrates the endeavours of chemists. Although the precise structural form in which each of its two hexoses occurs is understood, the problem of bringing together glucose and γ-fructose in such a manner as to present the opportunity for their condensation to a disaccharide still awaits solution. Meanwhile, further information is available [93]

[86] H. Hérissey and J. Cheymol, *Compt. rend.*, 1924, **178**, 1372; *A.*, i, 801.
[87] H. H. Schlubach and K. Maurer, *Ber.*, 1924, **57**, [*B*], 1686; *A.*, i, 1286.
[88] J. C. Irvine and H. S. Gilchrist, *J.*, 1924, **125**, 1.
[89] C. G. Tomecko and R. Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 2698; *A.*, 1924, i, 14.
[90] S. Ghosh, *J. Amer. Pharm. Assoc.*, 1923, **12**, 1080; *A.*, 1924, i, 659.
[91] E. Potel, *Bull. Soc. chim.*, 1923, [iv], **33**, 1459; *A.*, 1924, i, 15.
[92] H. Pringsheim and J. Leibowitz, *Ber.*, 1924, **57**, [*B*], 1576; *A.*, i, 1169.
[93] H. Colin and A. Chaudun, *Bull. Soc. Chim. biol.*, 1924, **6**, 625; *A.*, i, 1286.

confirming the presence of the glucose constituent in the α-form, and a useful method is devised which may prove valuable in the isolation of sucrose in small quantities in admixture with glucose and fructose. This depends on the observation [94] that the hexoses may be oxidised with yellow mercuric oxide to the sugar acids, and in contact with calcium carbonate, the sucrose evades hydrolysis and may be recovered and purified from acetic acid.

Sucrose is converted at its melting point into a mixture of glucose and lævulosan, and if this mixture is heated further at 185°/15 mm. until 5% of its weight is lost, the product is *iso*saccharosan, which can also be obtained on heating a mixture of glucosan and lævulosan. The constitution [95] assigned to *iso*saccharosan is



The treatment of this compound with cold 5% ammonia is said to lead to *iso*sucrose.

By submitting lactose to similar conditions of heating, it is transformed into lactosan, $C_{12}H_{20}O_{10}$, an amorphous powder which dissolves in water without displaying mutarotation.[96] In reaction with phenylhydrazine it yields lactosazone, and, on acetylation, gives lactose octa-acetate. Lactosan is said to be 5-galactosido-glucosan; it is polymerised to the compound $(C_{12}H_{20}O_{10})_4$ by heating briefly at 105° in presence of a trace of zinc chloride.

A reinvestigation of compounds of the glucal type such as lactal and glucal itself, which were first described by Fischer, has resulted in the better characterisation of these compounds and their preparation in a condition of greater purity. Several new transformations of a like kind have been effected, involving the isolation of *iso*lactal and the conversion of lactal into 5-galactosido-mannose, which is apparently a new disaccharide, giving the same osazone as lactose. The reduction of acetobromomaltose under conditions which produce glucal formation has led to the isolation of a derivative of maltal, from which another disaccharide, said to be 6-glucosido-mannose, is obtained [97] on oxidation with perbenzoic acid.

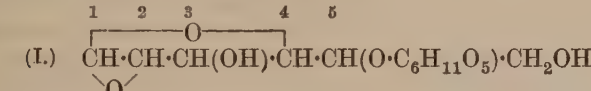
[94] S. Komatsu and M. Tanimura, *Mem. Coll. Sci. Kyōtō*, 1924, **7**, 161; *A.*, i, 713.

[95] A. Pictet and N. Andrianoff, *Helv. Chim. Acta*, 1924, **7**, 703; *A.*, i, 1045; compare i, 499; A. Pictet and P. Stricker, *ibid.*, p. 708; *A.*, i, 1046.

[96] A. Pictet and M. M. Egan, *ibid.*, p. 295; *A.*, i, 499.

[97] M. Bergmann [and, in part, H. Schotte, E. Rennert, S. Ludewig, and M. Kobel], *Annalen*, 1923, **434**, 79; *A.*, i, 265.

The need for an extension and standardisation of sugar nomenclature is recognised, and a proposal is made that, in describing the constitution of disaccharides, the hexose residue which retains its free reducing group in the biose complex should end with the suffix -ose, whilst the other hexose should be named as the glucoside constituent. Thus, lactose becomes 5-galactosido-glucose. In the case of a non-reducing disaccharide like sucrose, the use of the term glucosido-fructoside, or fructosido-glucoside, is advocated. Applying this system to trisaccharides, raffinose is described as galactosido-(glucosido-fructoside). It is further suggested that the terms anhydro-sugar, anhydrobiose may be employed when the reducing group is not implicated in the anhydride formation. Should the reducing group be involved, however, it is considered preferable to speak of the compound as a monose-anhydride or a biose-anhydride. The points of attachment of the internal oxide-ring may be represented by placing the numerals in brackets. For example, the compound (I) shown below is designated 5-galactosido-mannose-anhydride [1 : 4] [1 : 2



(I.)

Questions have been raised as to the purity of the acetobromomaltose obtained by Karrer's method, since the product gives a yield of only 30% of hepta-acetylmaltose. Pure acetobromomaltose is best prepared [98] by allowing maltose to remain in contact with acetyl bromide at 0° for 20 to 40 minutes. Material prepared by this method gives a yield of 70% of hepta-acetylmaltose on heating with acetic acid and sodium acetate

Polysaccharides.

Starch.—The investigation of the constitution of starch is seen to depend increasingly on the application of biological methods. In those cases where definite progress has been achieved along these lines, greater attention has been directed to the homogeneity of the materials and of the enzymes, and especially to the adoption of generally accepted standards by which the products of the reaction are characterised. One example may be quoted from the work of H. Pringsheim and his collaborators.[99] Starch hydrolysis

[98] H. Fischer and F. Kögl, *Annalen*, 1924, **436**, 219; *A.*, i, 498; compare E. and H. Fischer, *A.*, 1910, i, 716; Karrer, *A.*, 1921, i, 310, 313, 768.

[99] H. Pringsheim and K. Schmalz, *Biochem. Z.*, 1923, **142**, 108; *A.*, i, 106; O. Holmbergh, *Ark. Kemi, Min., Geol.*, 1923, **8**, No. 33, 1; *A.*, i, 691; *Biochem. Z.*, 1924, **145**, 244; *A.*, i, 691.

by the agency of maltase-free amylases is found to proceed beyond the supposed limiting value of 70—78% of maltose formation, and as much as a 96% yield of the latter has been obtained. In yeast, a complementary agent occurs which has the effect of pressing the hydrolysis of starch beyond the previously recognised limiting value obtainable with amylases, such as those of the saliva and the pancreas. This complementary agent reactivates very markedly old preparations of malt extract which have lost much of their amylolytic power, and the accelerating agent is itself destroyed by boiling.

Again, the methods of Ling and Nanji, commented on in last year's Report, of distinguishing between the content- and integument-materials of the starch granule have been freely recognised, and confirmation of their results is afforded in that these two materials are found to give rise respectively to a disaccharide and a trisaccharide.

The amylose and amylopectin separated by Ling and Nanji's procedure [1] were each subjected to depolymerisation and gave respectively a dihexosan (from amylose) and a trihexosan (from amylopectin).[2] Hitherto these compounds have been obtained as a mixture by submitting starch itself to depolymerisation by heating with glycerol.

Further evidence of this differentiation between the inner and the outer substances of the starch granule is adduced by the observation that the former, amylose, is converted in the cold, with concentrated hydrochloric acid, into amylobiose, a new disaccharide, whereas the outer material, amylopectin, yields under this treatment a trisaccharide, amylotriose, which forms an osazone.[3] On the other hand, as shown by Ling and Nanji, amylose is converted quantitatively into maltose under the influence of purified emulsin, or of amylases, but with amylopectin the reaction ceases when 65% has been converted into maltose. The unattacked residue of 35% in the amylopectin is recognised as trihexosan, which, since it can be further fermented with undialysed malt extract, appears not to be an essential component of the amylopectin molecule, but an "accidental" residue. Amylose is said to occur independently in nature and is shown to be identical with *iso*lichenin obtained from Iceland moss, since it gives rise to amylobiose, whilst amylopectin is considered to be identical with glycogen,

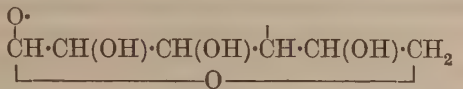
[1] A. R. Ling and D. R. Nanji, *J.*, 1923, **123**, 2666.

[2] H. Pringsheim and K. Wolfsohn, *Ber.*, 1924, **57**, [*B*], 887; *A.*, i, 714; compare *A.*, 1923, i, 899.

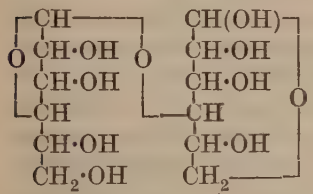
[3] H. Pringsheim [with A. Beiser, K. Wolfsohn, L. Leibowitz, and W. Kusenack], *ibid.*, p. 1581; *A.*, i, 1170; R. Kuhn, *Z. physiol. Chem.*, 1924, **135**, 12; *A.*, i, 692.

since the latter is transformed by cold concentrated hydrochloric acid into amylotriose.

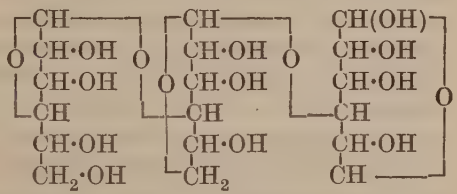
Amylobiose and amylotriose and also di- and tri-hexosan are all converted quantitatively into maltose by malt diastase. They are not attacked by the α-glucosidic enzyme, maltase, or by the β-glucosidic enzyme of emulsin. The most surprising result here involved is that of the quantitative formation of one biose, maltose, from a different biose and a triose. This is not to be regarded, however, as a reversible synthetic action of enzymes such as that shown to lead to maltose from glucose, but is most readily explained by the hypothesis that a glucose residue (I) readjusts the nature

(I.) 

of its oxide ring or is eliminated as a radical which unites with another similar residue to yield maltose. The following constitutional formulæ are proposed for amylobiose (II) and amylotriose (III)



(II.)



(III.)

Amylobiose, the new disaccharide, is also obtained by the cold hydrochloric acid treatment of α-tetra-amylose or β-hexa-amylose.[4]

That β-hexa-amylose cannot be identical with triamylose is proved by the conversion of the former on exhaustive methylation into the crystalline β-hexa(trimethylamylose), which, on hydrolysis, yields only 2 : 3 : 6-trimethyl glucose.[5]

Slightly divergent results are perhaps only to be expected at this early stage of so complex a problem, but a comparison of the products isolated from different preparations and by various workers would be greatly facilitated if all the available physical constants of the products were accurately determined and placed on record.

Another worker [6] has reported that the action of undialysed amylase solution on amylose leads to the isolation of a dihexosan

[4] H. Pringsheim and J. Leibowitz, *Ber.*, 1924, **57**, [*B*], 884; *A.*, i, 714; compare A., 1923, i, 899.

[5] J. C. Irvine, H. Pringsheim, and J. Macdonald, *J.*, 1924, **125**, 942.

[6] K. Sjoberg, *Ber.*, 1924, **57**, [*B*], 1251; *A.*, i, 1169.

which is probably identical with that described above. It yields a diacetate, and also a tetramethyl derivative, from which 2 : 3-dimethyl glucose is obtained on hydrolysis. Under similar treatment with this ferment, amylopectin yielded a trihexosan, probably identical with that isolated by Pictet and his collaborators [7] by heating potato starch with glycerol.

Amylopectins prepared from different starches differ in appearance, conductivity, viscosity, and in other properties of their aqueous solutions, as well as in their phosphorus content and acidity. The amylopectins from underground storage organs as in the potato, arrowroot, and tapioca, are distinct from those from seeds as in maize, rice, and wheat. These differences are maintained even in acid-treated starches. It is reported, however, that synthetic amylopectins prepared from different starches are closely analogous.[8]

Glycogen.—H. Pringsheim identifies glycogen with the amylopectin constituent of starch, and the identical behaviour of starch and glycogen on methylation, as well as the similarity of the methylated hydrolysis products, bears out this hypothesis. Glycogen has been exhaustively methylated [9] with methyl sulphate in presence of sodium hydroxide and yields a product containing 36·4% of methoxyl and having $[\alpha]_D$ + 179·8° in chloroform. This corresponds with the introduction of two to three methyl groups into each glucose residue. Either steric hindrance or physical condition militates against further alkylation. Hydrolysis of this product with methyl-alcoholic hydrogen chloride yielded the glucoside of butylene-oxidic 2 : 3 : 6-trimethyl glucose, identical with a specimen isolated from starch, cellobiose, and cellulose. A second product of cleavage was a dimethyl glucose of the butylene-oxide type, and this is possibly a 2 : 5-derivative.

Pectins.—The jelly-making substance of fruits has long been recognised as a valuable domestic adjunct, and the discovery of pectin in these juices was made many years ago by Braconnot. The combined investigations by Fremy, Scheibler, Herzfeld, Tollens, and others served to establish the fact that the pectins are carbohydrate derivatives possessing acid properties. Two more recent investigators, von Fellenberg and Ehrlich, have recognised the presence in pectins of methyl ester groups and galactose, and of the galactose analogue of glucuronic acid, namely, galacturonic acid, which is the intermediate oxidation product between galactose and mucic acid.

[7] A. Pictet and P. Stricker, *Helv. Chim. Acta*, 1924, **7**, 932; *A.*, **i**, 1288; A. Pictet and R. Salzmann, *ibid.*, p. 934; *A.*, i, 1288.

[8] M. Samec, M. Minaev, and N. Ronžin, *Koll. Chem. Beihefte*, 1924, **19**, 203; *A.*, i, 923.

[9] A. K. Macbeth and J. Mackay, *J.*, 1924, **125**, 1513.

On hydrolysis of pectins with alkali, methyl alcohol is eliminated, but *iso*propenyl groups may to some extent occupy the place of the methyl groups, especially in apple pectin, and so also may metallic residues.

Ehrlich describes [10] the naturally occurring pectin of plants as the "calcium magnesium salt of a complex anhydro-arabino-galactose-methoxyltetragalactonic acid," some units of which are loosely bound. Pectic acid is obtained by dissolving out the araban, and by eliminating the calcium and magnesium with dilute acids. The product still contains methoxyl residues and is spoken of as an ester-acid, but is regarded by Ehrlich as essentially a galactose-galacturonic acid, an equimolecular union of galactose and galacturonic acid analogous to the paired glucuronic acids which occur in the animal body.

At least three pectin substances have been definitely recognised: pectose (or protopectin), the parent substance; soluble pectin (or pectin); and pectic acid. The existence of protopectin has recently been questioned by Tutin. Of these three forms, protopectin is said to occur in succulent root vegetables and unripe fruits; soluble pectin in ripe fruits; and pectic acid in over-ripe fruits and vegetables. Progressive hydrolysis, either by enzymes or dilute acids, converts protopectin into soluble pectin and this into pectic acid. A similar degradation of pectins occurs in the processes of the natural or chemical retting of flax and hemp fibres.

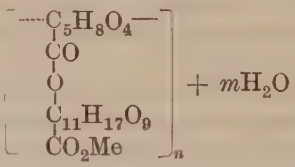
When fruit juices containing pectins are boiled with sugar and organic acids, the viscous solution sets to a jelly on cooling. Prolonged boiling, however, destroys this property, probably owing to the formation of pectic acid. Jelly formation is therefore a property neither of fully methoxylated pectin nor of pectic acid, but of the partly hydrolysed intermediate products.

The dried pulp of sugar-beet contains about 25% of pectin and constitutes an immense source of the raw material. The pectin of sugar-beet contains a glucuronic acid residue, and it is suggested that this acid is the intermediate stage in the formation of pentoses from hexoses in nature.[11] From the sugar-beet residues the crude pectin is obtained by treatment with dilute acids, and alcohol precipitates from this a dry, white powder, which dissolves in water to give solutions many times more viscous than those of gum arabic. It does not reduce Fehling's solution, but gives the naphtharesorcinol test for glucuronic acid. The latter acid is isolated after treatment of the purified pectin with 1% sulphuric acid at 130°.

[10] A useful résumé and a bibliography of the subject are given by W. H. Dore, *Ind. Eng. Chem.*, 1924, **16**, 1042.

[11] K. Smoleński, *Roczniki Chemji*, 1923, **3**, 86; *A.*, 1924, i, 16.

Two substances are recognised in the crude pectin. The portion insoluble in alcohol, or purified pectin, which contains *d*-galacturonic acid in considerable amount; and the alcohol-soluble portion, which is a polysaccharide consisting almost entirely of *l*-arabinose residues. The latter, araban, is lævorotatory; it readily undergoes hydrolysis and becomes dextrorotatory as the *l*-arabinose is formed. The original pectin of the sugar-beet is probably insoluble in water, dissolving, however, as hydrolysis proceeds, with the formation of the above two constituents. This hydrolytic process is found to occur rapidly in the presence of $N/200$-mineral acid. A constitutional formula for pectin has been suggested :



and it is considered probable that these substances occur in the plant as the result of oxidation of hexosans such as starch.

Lichenin.—The material known as reserve cellulose, or lichenin, occurs freely in the lichens and bears a somewhat near relationship to cellulose on the one hand, and to a constituent of starch on the other. It occurs in Iceland moss, from which it may be extracted with boiling water, and is a white powder, dissolving to a clear colloidal solution in hot water. Acetolysis proceeds much more slowly than with cellulose, and the yield of octa-acetylcellobiose is smaller.[12] A soluble lichenin is recognised which is attacked more readily than the ordinary, sparingly soluble form mentioned above. The similarity of lichenin to cellulose is said to be such as to connote little essential constitutional difference. The enzyme or enzymes occurring in the alimentary canal of the edible snail (*Helix pomatia*) has been provisionally called *lichenase*, since it ferments soluble lichenin to glucose in a few hours. Sparingly soluble lichenin is also vigorously attacked at first, but the rate is soon retarded. Cotton cellulose is attacked by lichenase, but sparingly and incompletely on account of its insolubility. The fermentation is said to depend on the dispersity of the substrate, the course of the reaction with soluble lichenin being at first unimolecular until the disappearance of the most highly dispersed particles.

Lichenase is closely related to cytase, but the latter contains enzymes which attack not only reserve celluloses, but also mannan

[12] P. Karrer, B. Joos, and M. Staub, *Helv. Chim. Acta*, 1923, **6**, 800; *A.*, 1923, i, 1182; P. Karrer, M. Staub, and J. Staub, *ibid.*, 1924, **7**, 159; *A.*, i, 373.

and galactan. A method of preparing lichenase free from the numerous enzymes which accompany it in the edible snail is given.[13]

Exhaustive methylation of lichenin with methyl sulphate leads to a product containing 41·9% of methoxyl compared with the usual maximum of 42—43% in the case of cotton cellulose. Methylated lichenin [14] dissolves in water to a colloidal solution, and resembles, in some respects, methylated hydrocellulose more than methylated cellulose, but, unlike the former, it does not depress the freezing point of water. Hydrolysis with 1% methylalcoholic hydrogen chloride gives rise to trimethyl- and dimethyl-methylglucosides in similar proportions to those obtained from fully methylated cellulose.

Since lichenin may be hydrolysed to glucose by malt extract and also yields octa-acetylcellobiose on acetolysis, it ought to be possible to show that malt extract is capable of hydrolysing lichenin first to cellobiose by the agency of a lichenase, and then to glucose by the agency of cellobiase; that is, to prove that lichenase and cellobiase are both present in malt extract. This speculation has been verified.[15] An attenuated malt extract obtained by keeping for three months, hydrolysed lichenin only to cellobiose, which was identified by its rotatory and reducing power and by the isolation of its osazone. Cellobiase evidently disappears from malt extract by long storage.

Lignin.—The processes which are operative in the plant leading to the slow oxidation of starch to pectins as the fruit matures, possibly find a parallel in other kinds of vegetation in the slow conversion of cellulose into lignin. An explanation of the formation of coal may also be furnished by the close study of the exceptional properties of lignin substances. Coal-like products are obtained with surprising rapidity by exposure, at relatively low temperatures, of wood tissue or of cellulose to the action of salts which are found in sea water. At 95°, magnesium chloride produces a marked change and hydrochloric acid is eliminated.[16]

The work of Bray and Andrews [17] on the chemical processes occurring during the bacterial decay of wood may, however, be cited in support of the hypothesis that the origin of coal is not chiefly traceable to the cellulose of dead vegetation but to the

[13] P. Karrer, M. Staub, A. Weinhagen, and B. Joos, *Helv. Chim. Acta*, 1923, **6**, 144; *A.*, i, 471.

[14] P. Karrer and K. Nishida, *ibid.*, p. 363; *A.*, i, 501; P. Karrer and M. Staub, *ibid.*, p. 928; *A.*, i, 1288.

[15] P. Karrer, M. Staub, and B. Joos, *ibid.*, p. 154; *A.*, i, 471; P. Karrer and M. Staub, *ibid.*, p. 916; *A.*, i, 1382; *ibid.*, i, 471; H. Pringsheim and J. Leibowitz, *Z. physiol. Chem.*, 1923, **131**, 262; *A.*, 1924, i, 233.

[16] C. G. Schwalbe and R. Schepp, *Ber.*, 1924, **57**, [*B*], 319; *A.*, i, 377.

[17] M. W. Bray and T. M. Andrews, *Ind. Eng. Chem.*, 1924, **16**, 137.

lignin. These authors have shown that in the space of 3 years the cellulose content of wood had decreased to 6%, whereas the lignin had practically resisted bacterial action. Schwalbe's experiments, showing that powerful dehydrating agents act on cellulose to form a substance resembling coal, are held to be invalid as an argument in support of his hypothesis, because the conditions of the experiment differed greatly from those prevailing in nature. The view [18] which is preferred is that dead vegetation would be rapidly attacked by bacterial decay with consequent destruction of the cellulose, and that the lignin which survives this attack is converted into coal. The above experiments with solutions of mineral chlorides both on lignin- and cellulose-containing substances indicate, however, that the truth lies probably somewhere between these two points of view.

Lignin is far less stable than cellulose when heated with aqueous alkali. It is observed [19] that, whilst at 300° cellulose undergoes complete dissolution, partly decomposing with production of much carbon dioxide, lignin is decomposed by 9·5*N*-potassium hydroxide at 300° with the formation of phenols and adipic acid, and by 10*N*-sodium hydroxide at 250° with the production of succinic and oxalic acids. Autoxidation of lignin occurs in presence of sodium hydroxide, yielding humic acids as well as the above, possibly also *iso*phthalic acid, and, in addition, acetic, formic, and carbonic acids. Cellulose is attacked to a lesser degree and similar differences are observed in the comparative oxidation of lignin and cellulose under pressure; the latter tends to form aliphatic acids, whilst lignin produces, in addition, aromatic acids. Its ready nitration is in harmony with the supposed phenolic structure of lignin. The tar obtained by destructive distillation of lignin appears to contain no optically active compounds in its aqueous extracts, whereas lævoglucosan is isolated from cellulose under parallel conditions. It is therefore clear that the polysaccharide character of cellulose is largely modified in lignin. The *cyclo*saccharides or cycloses in the latter may be regarded as intermediate links capable of uniting partly with true carbohydrates and directly with each other.[20] The presence of hydroaromatic rings in lignin, and its, as yet undetermined, position between the aliphatic and aromatic compounds, provide a stimulus to speculation and investigation. The methyl ether of inositol is a constituent of the sap of certain conifers, and from inositol are obtainable several of the aromatic and aliphatic derivatives detected in the cleavage products of lignin.

[18] F. Fischer, *Brennstoff-Chem.*, 1924, **5**, 132; *A.*, i, 715.

[19] F. Fischer and H. Tropsch, *Ber.*, 1923, **56**, [*B*], 2418; *A.*, 1924, i, 148; E. Heuser and F. Herrmann, *Cellulosechem.*, 1924, **5**, 1; *A.*, i, 376.

[20] E. Strupp, *Cellulosechem.*, 1924, **5**, 6; *A.*, i, 376.

From flax lignin, by digestion with dilute alkali, a homogeneous product (I) has been isolated,[21] and this passes on acetylation into (II) and by methylation with methyl sulphate into the methyl lignin (III).

(I.) $C_{40}H_{30}O_6(OH)_5(OMe)_4 \cdot CHO$; (II.) $C_{40}H_{30}O_6(OMe)_4(OAc)_5 \cdot CHO$;
(III.) $C_{40}H_{30}O_6(OH)_2(OMe)_7 \cdot CHO$.

The presence of one aldehyde group in lignin is deduced from the action of Fehling's solution and of phenylhydrazine. The product (II) is insoluble in cold, dilute alkali, but is readily hydrolysed by boiling water, indicating that the acidic properties of the lignin are to be ascribed to phenolic hydroxyl groups. The product (III) is insoluble in alkali hydroxide and resistant to hydrolysis and acetylation, pointing to some difference between the remaining hydroxyl groups in lignin and those in its derivatives. Cold nitric acid introduces three nitro-groups into lignin, giving the red compound, $C_{42}H_{39}O_{22}N_3$, which contains one methoxyl group and behaves as an aromatic compound. Into this, six acetyl groups can be admitted, giving acetylnitrolignin.

In the absence of sunlight, chlorine and bromine substitution occur with lignin, giving chlorolignin, $C_{40}H_{20}O_8Cl_{12}(OMe)_2(OH)_5 \cdot CHO$, and the corresponding bromolignin, both of which are soluble in alkali and have suffered partial demethylation. They are not affected by hot nitric acid and are only partially dehalogenated by boiling with sodium hydroxide. The remaining halogen atoms are thus attached to aromatic nuclei. The halogenated and acetylated lignins, as well as the acetylnitrolignins, are hydrolysed with differing degrees of readiness.

Comparison of these results with those of Cross and Bevan, Klason, and of Bechmann and Liesche, shows that the lignins from jute, flax and pine are not identical, but that those from flax and winter rye straw are closely related.

The process of digesting spruce wood with a 7% solution of sulphurous acid, free from sulphuric acid, is shown to be attended by a lower degree of sulphonation than in the case of the digestion with calcium hydrogen sulphite. The process is accompanied, however, by a pronounced degradation of the cellulose.[22] Lignosulphonic acid has been separated [23] from the products and contains the characteristic groups represented in the formula

$$C_{21}H_{15}O_2(SO_3H)(OH)_2(CH_2 \cdot OH)(CH \cdot OH)(CHO)(OMe)_2.$$

Its reactions show that it consists almost entirely of a substance

[21] W. J. Powell and H. Whittaker, *J.*, 1924, **125**, 357.

[22] C. F. Cross and A. Engelstad, *J. Soc. Chem. Ind.*, 1924, **43**, 253T; *A.*, i, 1048.

[23] C. Dorée and L. Hall, *ibid.*, p. 257; *A.*, i, 1048.

of Klason's α-type (aldehydic) of lignone. With dilute nitric acid oxidation of the constituent groups occurs with the following result :

$$C_{22}H_{22}O_5(NO_2)_2(OH)_3(CO)(CO_2H)_2(OMe).$$

This nitro-compound, on reduction, shows no resemblance to the aromatic type, and the behaviour of the substance recalls that of some unsaturated terpenes of the cholesterol series. The C_{20} nucleus of lignone is thus probably hydroaromatic in character, consisting of a reduced ring complex resembling the reduced benzophenanthrene hydrocarbon formulated by Schrauth.[24]

Cellulose.

The name cellulose is applied to many nearly-related products differing in origin and sometimes also in properties and chemical constitution. Cotton cellulose may be regarded as the pure standard product, and the problem has arisen as to the homogeneity of many other varieties.

Spruce wood appears to contain cellulose of two types,[25] one resistant to a solution of sodium hydrogen sulphite containing 1·83% of hydrochloric acid and heated to 98°, and the other resistant to a similar solution containing only 0·73% of hydrochloric acid. The type of cellulose which is unaffected by the stronger acid solution corresponds to crystalline cellulose, and the other type to amorphous cellulose. It is proposed to define cellulose as the substance corresponding to the latter type, namely, that which is resistant only to the weaker acid, since cotton cellulose is attacked by the stronger acid solution.

To return to the occurrence of the two types in spruce wood, it is observed that in the natural condition in the plant cell the crystalline cellulose protects the amorphous from the action of the stronger acid, until the cells are mechanically ruptured by rasping, when the protection ceases. The degree of protection afforded by the crystalline variety varies in different species of wood, and is less complete in beech wood than in spruce.

The difference in behaviour exhibited by cotton cellulose and by esparto cellulose in contact with highly concentrated hydrochloric acid is very marked. Whilst from the former a 70% yield of glucose could be isolated in the form of a derivative, the esparto cellulose solution became highly coloured and evolved quantities of furfural.[26] The amount of furfuraldehyde produced corresponds with the presence of 18·5% of pentosan in the dry esparto cellulose. This pentosan can be completely extracted from cellulose of this origin

[24] W. Schrauth, *Z. angew. Chem.*, 1923, **36**, 149; *A.*, 1923, i, 443.
[25] P. Klason, *Papier-Fabr.*, 1924, **22**, 373; *A.*, i, 1289.
[26] E. L. Hirst and D. R. Morrison, *J.*, 1923, **123**, 3226.

by boiling with 12% sodium hydroxide and is identified as xylan, which readily hydrolyses to xylose. The remaining 81·5% of the esparto cellulose is identical with cotton cellulose,[27] since it gives, on acetylation (acetolysis), cellobiose octa-acetate, and, on methylation, the same trimethyl derivative as cotton cellulose. 2 : 3 : 6-Trimethyl glucose was isolated by the hydrolysis of each of these methyl celluloses.

Degradation of cotton cellulose with dilute sulphuric acid (5%) begins to be appreciable at 70° and hydrocellulose is one of the products. The formation and chemical behaviour of this substance have been closely studied.[28]

Cellulose, in cuprammonium solutions, undergoes no hydrolytic decomposition. The copper is present as an optically active complex anion and the kation is an ammine. The maximum rotation is attained immediately on solution of the cellulose. The solutions have been examined from the point of view of mass action, and the molecular complexity of the dissolved cellulose has been determined. Equations illustrating the formation of cellulose–cuprammonium solutions have been completely developed,[29] as also those for similar solutions of other carbohydrates.

A further study of the acetyl derivatives of cellulose has been undertaken with the object of determining the molecular weight of the carbohydrate, since it is established that the formation of what is known as cellulose triacetate A does not change the polymerised condition of the original substance. Pure unchanged cellulose can, indeed, be recovered from this compound.

Dried cotton cellulose does not react with dry acetyl chloride, but if 4—5% of moisture is present and the reactants are shaken in contact for 4 days at 17—20°, a 92% yield of crude triacetate A is obtained, and treatment with chloroform leads to the pure compound, which is a colourless powder. Variation of these conditions gives rise to cleavage by-products in considerable quantities, such as cellodextrinacetate, and derivatives of the disaccharide, cellobiose. Some of the cellulose acetates previously described as homogeneous contain these and other impurities. Cellulose triacetate A melts at 270—275°, and is lævorotatory in chloroform and dextrorotatory in glacial acetic acid. In phenol, its molecular weight has the value 2380—3350. Hydrolysis to the regenerated, unchanged cellulose is effected with cold *N*-methyl-alcoholic sodium hydroxide. The product, cellulose A, is a white powder having

[27] J. C. Irvine and E. L. Hirst, *J.*, 1924, **125**, 15.

[28] H. Gault and B. C. Mukerji, *Compt. rend.*, 1924, **179**, 402; *A.*, i, 1048.

[29] K. Hess, W. Weltzien, and E. Messmer, *Annalen*, 1923, **435**, 1; *A.*, 1924, i, 142.

$[\alpha]_D$ −12·4° in 2*N*-sodium hydroxide. It is shown by *X*-ray analysis to be crystalline, and its rotatory power in cuprammonium solutions establishes its structural identity with the original cotton cellulose used.

If acetic anhydride mixed with acetyl chloride be used in the acetylation of cellulose, an acetate is obtained which, on deacetylation, gives a regenerated cellulose less soluble in alkali than cellulose A. The by-product previously mentioned as occurring frequently, namely, cellodextrinacetate, is more soluble in the usual solvents than cellulose triacetate A, and gives a molecular weight value in phenol of 1260—1480. By deacetylation, dextrin is formed as a white powder, which reduces Fehling's solution.

The experimental procedure leading to the methylation of sparingly soluble polysaccharides by the agency of methyl sulphate has, in the past, involved the use of concentrated alkali in contact with the carbohydrate. These conditions differ materially from those which are usually applied to the water-soluble sugars, the methylation of which is usually conducted in an almost neutral medium until nearly the whole of the methyl groups have been introduced.

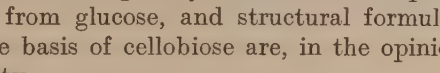
Doubt has now been expressed as to the value of the experimental results [30] obtained by Denham and Woodhouse and by Irvine and Hirst by the methylation of cellulose in strong solutions of alkali. It is suggested that the alkali has a definite action on cellulose at the temperature of methylation. Cellulose A, as is pointed out by Hess and his co-workers, is so altered by warming with dilute alkali that it reduces Fehling's solution and is no longer precipitated on acidification. If this change occurred during the process of methylation, the result would be masked owing to the rapid methylation of the exposed reducing group. Hydrated barium hydroxide, however, has no effect on cellulose A, and methylations conducted by substituting this reagent for alkali hydroxide may be assumed to proceed without the introduction of structural changes. The product obtained in this way was a yellow glass (OMe = 30·40%), insoluble in, and unaffected by, alkali, and, on further methylation with sodium hydroxide and methyl sulphate, gave trimethyl cellulose A (OMe = 42·43%). The results obtained from the hydrolysis of this product will be awaited with interest.

Acetylated cellulose A is partly converted by acetyl bromide, containing hydrogen bromide, into acetobromocellobiose, but accompanying this usual product there is a new acetobromoglucose. This new glucose derivative is converted into acetobromo-

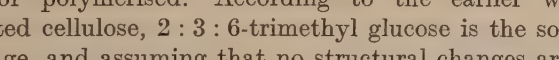
[30] *J.*, 1913, **103**, 1735; 1921, **119**, 77; 1923, **123**, 518.

cellobiose by the further action of acetyl bromide and hydrogen bromide. Deacetylation of the new variety of acetobromoglucose proceeds normally with alcoholic ammonia, but with acids the bromine is eliminated and celloglucosan is obtained, which can be converted quantitatively into α-methylglucoside. These results indicate that cellulose can be transformed into a derivative of glucose (the new acetobromoglucose) without the intermediate formation of cellobiose, and therefore it is considered no longer necessary to regard the latter as a genuine cleavage product of cellulose. Cellobiose is consequently assumed to be a product of reversion synthesis from glucose, and structural formulæ assigned to cellulose on the basis of cellobiose are, in the opinion of Hess, of doubtful validity.

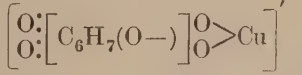
In their survey of this work occupying 144 pages in the *Annalen*, Hess and his collaborators conclude that cotton cellulose is built up from glucose anhydride units which are associated, not condensed or polymerised. According to the earlier workers on methylated cellulose, 2 : 3 : 6-trimethyl glucose is the sole product of cleavage, and assuming that no structural changes are involved in their method of procedure, the cellulose unit would be



At variance with this formula are the results already quoted as to the action of hydrogen bromide on cellulose triacetate A. Hess, Weltzien, and Messmer prefer to represent cellulose as the formula



Its dissolution in cuprammonium solution, which effects saturation of the partial valencies involved in the association of the cellulose units, may be expressed as giving rise to the ion :



The above cellulose formula is held to explain the amphoteric character of this carbohydrate and also its behaviour towards neutral salts such as zinc chloride. Natural cotton cellulose may contain as its crystal unit, as deduced from *X*-ray analysis, four $C_6H_{10}O_5$ residues associated together.

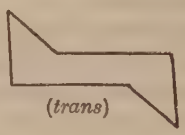
W. N. Haworth.

Part II.—Homocyclic Division.

Stereoisomerism. Mohr's Theory of Strainless Rings.

Evidence has recently been brought forward to show that the strain in large polymethylene rings (*e.g.*, the *cyclo*heptane ring) may be relieved by the twisting of the ring into a multiplanar configuration.[1] The theory of strainless configurations was first advanced by H. Sachse.[2] In the simplest case to which it can be applied, the *cyclo*hexane ring, there are two strainless forms (for convenience termed "*cis*" and "*trans*"), each of which can be considered to occupy three planes:

(*cis*)

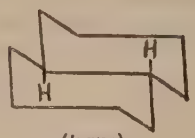


(*trans*)

*cyclo*Hexane derivatives, however, do not show the isomerism to which these formulæ should give rise, and from this it must be inferred either that this relief of strain does not take place, or that strainless forms represent phases only of the contortions of the molecule. The latter alternative seems the more probable, as the two forms are interconvertible by a process involving simultaneous rotations (with slight strain) around the single bonds.

E. Mohr[3] observed, however, that the fusion of two strainless *cyclo*hexane rings to give decahydronaphthalene could take place in two ways giving rise to isomerides the existence of which had previously been considered impossible. One contains two six-membered rings united by the *cis*-valencies of their common carbon atoms; the second, and more remarkable, contains a union by

(*cis*)

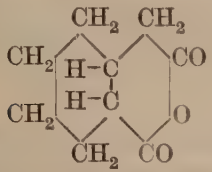


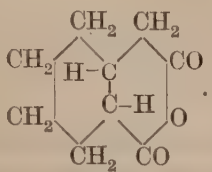
(*trans*)

trans-valencies. There is no question here of interconversion by twisting or simultaneous rotation around the bonds, for, although by this process variations of each formula can be produced, the two rings lock one another in such a way as to prevent interconversion of the types: the formulæ, in fact, represent stable isomerides.

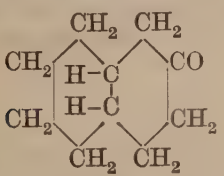
[1] *Ann. Reports*, 1923, **20**, 103.
[2] *Ber.*, 1890, **23**, 1363; *A.*, 1890, ii, 1386.
[3] *J. pr. Chem.*, 1918, [ii], **98**, 315.

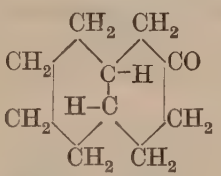
The first experimental evidence in favour of this theory was obtained by A. Windaus, W. Hückel, and G. Reverey,[4] who showed that the *trans*- as well as the *cis*-form of hexahydrohomophthalic acid gives a stable anhydride :


(*cis*)

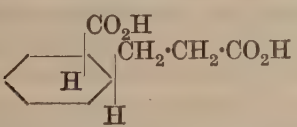

(*trans*)

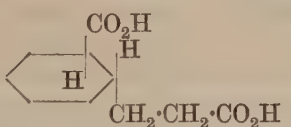
Hückel then discovered [5] that the two decahydro-β-naphthols (which had been investigated by Mascarelli and Recusani,[6] and were evidently regarded by them as ordinary geometrical isomerides related like tropine and ψ-tropine), on oxidation with chromic acid, gave different ketones. This is unaccountable on the basis of the ordinary theory of plane rings, but is readily explained by means of Mohr's theory :





The two ketones, on oxidation with permanganate, yield, as they should, the ordinary *cis*- and *trans*-forms, respectively, of 1-carboxy*cyclo*hexane-2-propionic acid :





and on reduction by Clemmensen's method give two decahydronaphthalenes differing by 8° in their boiling points.[7] An examination of their physical constants indicated that the contradictory boiling points and densities previously recorded for decahydronaphthalene, prepared by reduction of naphthalene, were due to the occurrence of mixtures of *cis*- and *trans*-forms. This has been proved in the case of technical decahydronaphthalene by W. Borsche

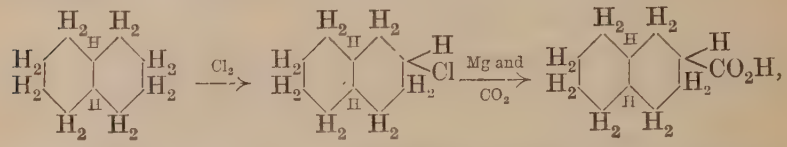
[4] *Ber.*, **1923**, **56**, [*B*], 95; *A.*, 1923, i, 220.

[5] *Nach. K. Ges. Wiss. Göttingen*, 1923, 43; *A.*, 1924, i, 31.

[6] *Atti R. Accad. Lincei*, 1911, 20 (v), **2**, 223; *A.*, 1912, i, 761.

[7] Compare also F. Eisenlohr and R. Polenske, *Ber.*, 1924, **57**, [*B*], 1639; *A.*, **i**, 1291.

and E. Lange,[8] who first converted Hückel's *cis*- and *trans*-decahydronaphthalenes into their respective carboxylic acids :



and then identified both of these in the mixture of acids produced in the same way from the technical hydrocarbon. R. Willstätter and F. Seitz [9] further established the fact that, whereas decahydronaphthalene prepared by means of platinum black consists essentially of the *cis*-hydrocarbon, the reduction of naphthalene with nickel and hydrogen at 160—162° yielded principally the *trans*-isomeride.

So far, then, as concerns decahydronaphthalene and β-ketodecahydronaphthalene, Mohr's theory may be regarded as established, but there are many obvious consequences which still await experimental verification. Thus there should be four stereoisomeric α- or β-monosubstitution products of decahydronaphthalene (all optically resolvable) :

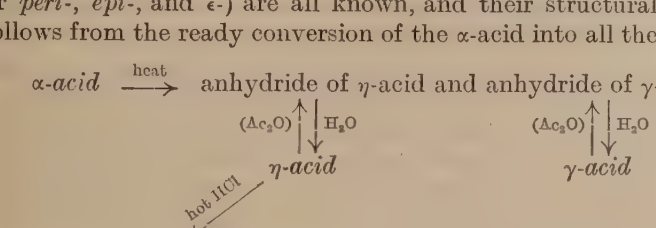
but hitherto no more than two have been obtained. Again, there should be five inactive stereoisomeric, fully hydrogenated anthracenes, two of which should be optically resolvable, and sixteen stereoisomeric α- or β-monosubstitution products (all resolvable); also six isomeric fully hydrogenated phenanthrenes, of which four should be resolvable, and sixteen of each of the five structurally different monosubstitution products (all resolvable),—significant consequences for workers in the field of the higher terpenes, the structures of which are now known to be based on the hydronaphthalene and hydrophenanthrene nuclei (p. 99).

cyclo*Butane Derivatives*.—A more conventional, but nevertheless difficult, stereochemical problem has been worked out in connexion with *cyclo*butane derivatives of type (I). Compounds of this class should exist in five geometrically isomeric forms. The first member of the group to have its five forms isolated and their configurations

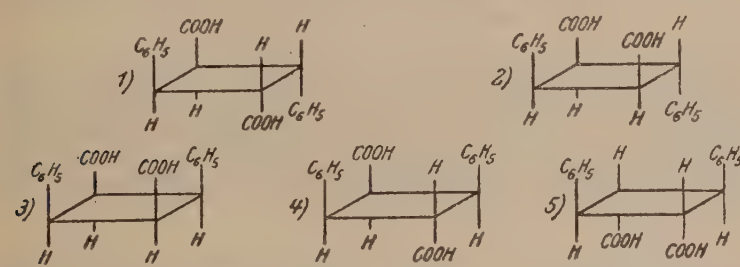
[8] *Annalen*, 1923, **434**, 219; *A.*, 1924, i, 32.
[9] *Ber.*, 1924, **57**, [*B*], 683; *A.*, i, 628.

assigned was the acid (II).[10] This year, the investigation of a second, and very interesting, case has been completed, namely, that of truxillic acid (III), which is formed by the self-addition of cinnamic acid.

The five truxillic acids (distinguished by the prefixes α-, γ-, η- or *peri-*, *epi-*, and ε-) are all known, and their structural identity follows from the ready conversion of the α-acid into all the others.[11]



If, now, the five possible structures be examined it will be seen that they can be divided into two groups :



Those with phenyls in the *trans*-position, formulæ (1) and (2), should lead to optically resolvable anilic acids; whilst those with *cis*-phenyls should give non-resolvable anilic acids. Applying this criterion, it is found that the α- and γ-acids belong to the first class, and the η-, *epi-*, and ε-acids to the second.[12] Consideration of the relative stability and ease of anhydride formation of the members of each group (compare the above interconversion scheme) then suffices for the definite allocation of the formulæ : (1) = α, (2) = γ, (3) = η, (4) = *epi*, and (5) = ε.

[10] C. K. Ingold, E. A. Perren, and J. F. Thorpe, *J.*, 1922, **121**, 1765.

[11] H. Stobbe and F. Zschoch, *Ber.*, 1923, **56**, [*B*], 676; *A.*, 1923, i, 337. R. Stoermer and F. Bacher, *ibid.*, 1924, **57**, [*B*], 15; *A.*, i, 400.

[12] R. Stoermer, *ibid.*, 1923, **56**, [*B*], 1683; *A.*, 1923, i, 929.

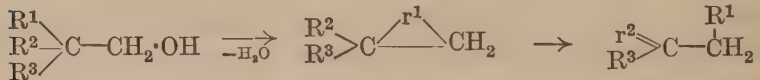
In addition to the truxillic acids a series of structural isomerides termed truxinic acids, having the formula

$$\begin{matrix} C_6H_5\cdot CH\text{—}CH\cdot CO_2H \\ C_6H_5\cdot CH\text{—}CH\cdot CO_2H \end{matrix}$$

are produced from cinnamic acid by additive ring synthesis;[13] but the stereochemical problem here involved is less advanced, as, of the six possible forms, four only (the β-, δ-, ζ-, and *neo*-acids) have so far been isolated.

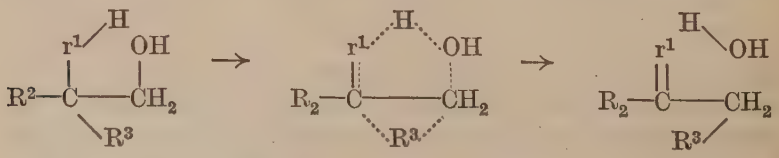
The Mechanism of the Wagner Rearrangement.

Two types of view have been expressed with regard to the mechanism of the rearrangement which so frequently accompanies the dehydration of *tert.*-alkyl carbinols. One hypothesis, upheld notably by Ruzicka,[14] postulates the closure and the fission in a different direction of a *cyclo*propane ring. The essential feature of this theory is that the hydrocarbon radical supplying the hydrogen eliminated as water (R^1 in the formulæ which follow) is the radical which undergoes transference to the adjoining carbon:



$$(R^1 = r^1H, \quad R^2 = r^2H)$$

The second hypothesis has been proposed in several forms, involving partial valencies,[15] free valencies,[16] or ions,[17] but the common requirement of all of them is that the radical supplying the hydrogen eliminated as water is *not* the one transferred. For example, using the partial valency hypothesis, the reaction may be formulated thus:



[13] M. Reimer (*J. Amer. Chem. Soc.*, 1924, **46**, 783; *A.*, i, 642) has shown that the conversion of methyl styrylglyoxylate, CHPh:CH·CO·CO_2Me, into *cyclo*butane derivatives by self-addition also occurs in both possible ways, and the same is probably true of the self-addition of coumarin (A. W. K. de Jong, *Rec. trav. chim.*, 1924, **43**, 316; *A.*, i, 644).

[14] L. Ruzicka and Fr. Liebl, *Helv. Chim. Acta*, 1923, **6**, 267; *A.*, 1923, i, 475.

[15] R. Robinson, *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4, 1.

[16] M. Tiffeneau, *Compt. rend.*, 1906, **143**, 684; *A.*, 1906, i, 39; J. Bredt, *Wüllner-Festschrift, Leipzig*, 1905, 123.

[17] H. Meerwein and R. Wortmann, *Annalen*, 1924, **435**, 190; *A.*, i, 188.

Three reasons have been given against the former view.

(*a*) In cases in which the intermediate ring compound can be prepared it is often found to be too stable to undergo the fission reaction under the conditions in which this is supposed to occur.[18]

(*b*) Instances are known in which optical activity is retained during the transformation, although the postulated intermediate ring compound is structurally incapable of optical activity.[19]

(*c*) Although the structure of the product does not usually differentiate between the mechanisms when water is eliminated, the analogous change in which bromine is eliminated by the use of a metal can only be interpreted by means of the second mechanism.[20]

Of course there are replies to all these arguments. As to (*a*) and (*b*), it might be said that considerations relating to isolated intermediate compounds do not apply to these substances in the "nascent" condition; and as to (*c*) it might be doubted whether the change in which bromine is eliminated is really analogous. But to most chemists, probably, these objections would appear weak, and on the whole the available evidence may be regarded as tending against the cycloid theory, although it does not finally disprove it.

Turning to the second hypothesis, it should first be observed that the various forms in which it has been advanced may not be so mutually antagonistic as might perhaps appear. From the investigation of triarylmethyls it is known (compare p. 115) that the production of free valencies and ions may be merely different manifestations of the same structural condition, this condition depending on a peculiar distribution of residual affinities. It therefore seems possible that, although in the great majority of cases the mutual attraction of the two parts of the molecule ultimately eliminated may cause an altered distribution of affinity and the consequent migration of a group, there may be special structures in which the natural distribution of affinity (apart from any tendency towards an elimination) is such as to loosen one of the attached groups, and give rise, under suitable conditions, to isomeric change dependent on the formation of a free valency or an ion.

It has recently been found that the Wagner change may occur without any elimination, and in cases in which there is little likelihood of an addition of water and its subsequent splitting off. It

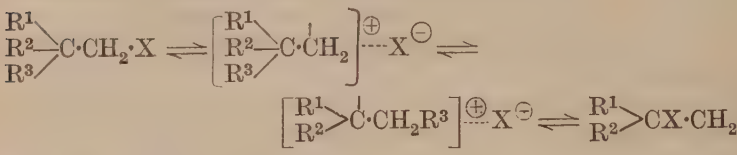
[18] H. Meerwein and K. van Emster, *Ber.*, 1920, **53**, [*B*], 1815; *A.*, 1920, i, 855.

[19] *Idem*, *ibid.*

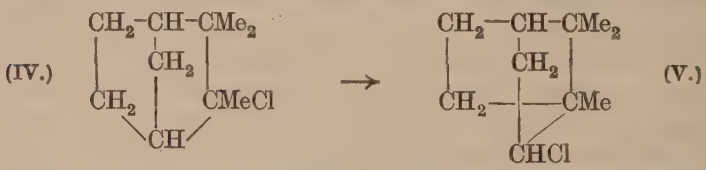
[20] C. K. Ingold, *J.*, 1923, **123**, 1706.

is significant that instances of this kind have been found amongst structures in which there is independent evidence of the possibility of ionisation, and that the changes are facilitated by the use of a dissociating solvent. This suggests that the explanation is to be sought in the ionic hypothesis, but at the same time the fact that this type of isomeric change appears to be *confined* to the structures in which there is evidence of ability to ionise seems to indicate that the ionic hypothesis should be applied only to such cases.

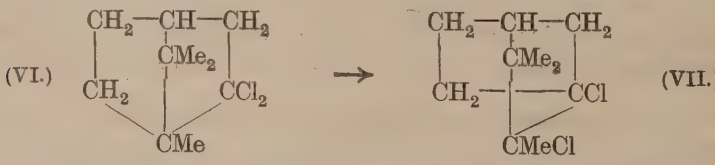
The ionic hypothesis may be formulated thus :



The cases which most clearly favour it belong to the camphane series, certain of the halogen compounds of which closely resemble in many of their reactions the triarymethyl halides, and to this extent are similar to acyl, rather than to alkyl, halides. Thus bornyl chloride (V) and camphene hydrochloride (IV) readily yield ethers on treatment with alcohols,[21] just as does triphenylmethyl chloride. Since triphenylmethyl chloride is known to be measurably ionised in solvents with a sufficiently high dielectric constant, the possibility of incipient ionisation in bornyl chloride and in camphene hydrochloride must be admitted; and it is found,[22] as would be expected from the ionic hypothesis, that the isomeric change (IV) ⟶ (V) readily takes place, in the presence, for instance,

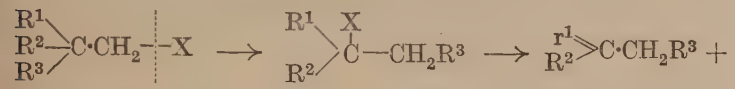


of cold alcoholic hydrochloric acid. Again 2 : 2-dichlorocamphane (VI) changes into α-chlorocamphene hydrochloride (VII) (which, under the conditions employed, loses hydrogen chloride, giving α-chlorocamphene) on treatment with potassium acetate in phenol solution :[23]

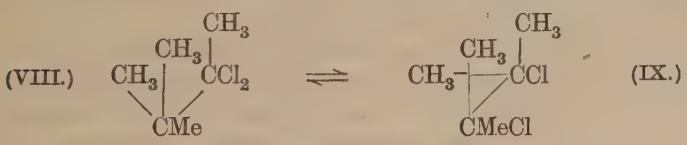


[21] H. Meerwein and L. Gérard, *Annalen*, 1924, **435**, 174; *A.*, i, 186.
[22] *Idem, ibid.* [23] H. Meerwein and R. Wortmann, *loc. cit.*

It should be said that Meerwein and Wortmann do not adopt the view that the ionic theory is peculiarly applicable to these halogen camphanes: they apply their theory to *all* cases of the Wagner rearrangement, even those in which there is elimination. In their opinion the elimination of water in the dehydration of a *tert.*-alkyl carbinol is not the "driving force" of the rearrangement, but is a subsequent occurrence, the real migration occurring within the ion remaining after the hydroxyl group has been removed by electrolytic dissociation. The function of the acid used to bring about the change is to esterify the hydroxyl group, it being assumed that the ester so produced would be ionisable as shown below (X = acid radical):



According to this theory, therefore, the rearrangements of the halogen camphanes correspond with Wagner dehydrations of carbinols by means of hydrochloric acid, and the fact that these "hydrochloric esters" are capable of isomeric change is regarded as justifying the general hypothesis. Now the "hydrochloric esters," (VIII) and (IX), of pinacolin and pinacol are related to one another precisely like the chlorocamphanes, (VI) and (VII), and might be expected, therefore, to be as readily interconvertible.



The change cannot be effected in either direction,[24] however, and this, taken in conjunction with the fact that there is here no independent evidence of tendency to ionise, is perhaps an indication that special structural conditions are necessary for rearrangement by the ionic mechanism.

The Structure of the Sesquiterpenes.

Although many of the sesquiterpenes have long been known, attempts to achieve order in their chemistry have, until recently, met with little success. With the work of Ruzicka and his colleagues, however, this new field has been entered. Structural types have been established, and the constitutions of some members of each of them exactly determined; more important still, order

[24] H. Meerwein and R. Wortmann, *loc. cit.*

can be seen amongst the facts. Rational sesquiterpene chemistry may now be said to have definitely entered on its career; and, as future progress may be expected to be rapid, a summary of the present position seems desirable.

More than 300 naturally occurring sesquiterpene products have been described, but all these are not equally well characterised, and it is possible that some are identical or contain identical constituents, and that others are stereoisomeric forms (p. 94) of the same structural individual. Amongst the best known members of the series are

Cadinene, from oil of cubebs.
Caryophyllene, from carnation oil and copaiba oil.
Santalene, from sandal-wood oil.
Selinene, from celery-seed oil.
Zingiberene, from ginger oil.

In addition to these, there are numerous related alcohols, such as

Calamenol, $C_{15}H_{24}O$, from calamus-root oil.
Cadinol, $C_{15}H_{26}O$, from galbanum oil.
Eudesmol, $C_{15}H_{26}O$, from eucalyptus oil.
Farnesol, $C_{15}N_{26}O$, from musk-seed oil and acacia-blossom oil.

The first of these compounds to have its structure established was the open-chain alcohol, farnesol, which was proved by M. Kerschbaum,[25] in 1913, to have the structure

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}OH.$$

Most that is known about the hydrocarbons themselves, however, has been the outcome of the work carried out by Ruzicka and his collaborators since 1921, Semmler's earlier conclusions having undergone considerable modification at the hands of these investigators.

O. Wallach first suggested (1887) that the naphthalene nucleus might be the basis of sesquiterpene structure,[26] and F. W. Semmler [27] (1903) developed this idea. Both investigators based their speculations on the principle of division into isoprene units, $\begin{matrix}C\\C\end{matrix}\!>\!C{-}C{-}C$, a principle to which there has hitherto been no established exception amongst terpenes.

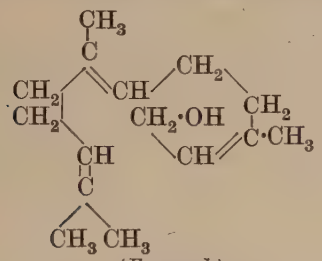
Until 1922, however, no definite naphthalene derivative had been identified amongst the degradation products of sesquiterpenes. But A. Vesterberg's proof (1903) that abietic acid (a diterpene acid, $C_{20}H_{30}O_2$), on heating with sulphur, yielded retene [28] (1-methyl-

[25] *Ber.*, 1913, **46**, 1732; *A.*, 1913, i, 739. [26] *Annalen*, 1887, **239**, 49.
[27] *Ber.*, 1903, **36**, 1038. [28] *Ibid.*, p. 4200; *A.*, 1904, i, 151.

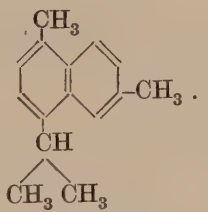
7-*iso*propylphenanthrene) might have been regarded as suggesting the following regularity :

Terpenes, C_{10}, based on benzene nucleus.
Sesquiterpenes, C_{15}, based on naphthalene nucleus.
Diterpenes, C_{20}, based on phenanthrene nucleus.

Using Vesterberg's sulphur method, Ruzicka and his collaborators dehydrogenated a number of sesquiterpenes and related alcohols. Most of them, including cadinene, zingiberine, and calamenol, gave the same hydrocarbon, $C_{15}H_{18}$, which was evidently a naphthalene derivative, and was termed "cadalene."[29] Adopting the hypothesis that farnesol might be related to cadinene as the simple open-chain terpene–alcohol geraniol is to dipentene, the following probable structure for cadalene was reached :



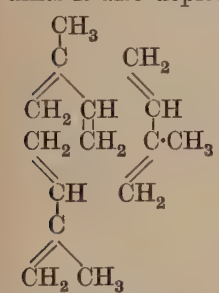
(*Farnesol.*)



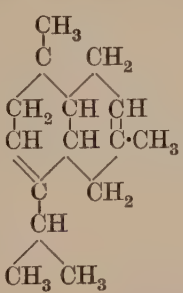
(*Cadalene.*)

Cadalene was then synthesised, and this hypothesis confirmed.[30]

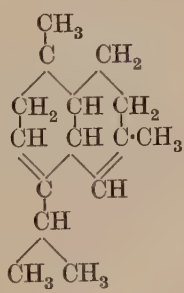
As to the positions of the two double linkings present in cadinene, reduction experiments prove that they are not conjugated, and by combining this result with the evidence from ozonolysis, it is shown that cadinene may be represented by either or both of the following formulæ (the formation of the carbon framework from isoprene units is also depicted) : [31]



(3 mols. *Isoprene.*)



(*Cadinene.*)

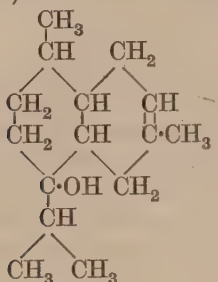


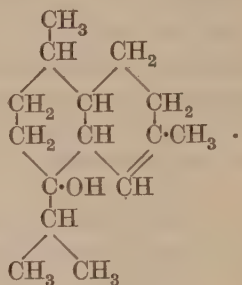
[29] L. Ruzicka, *Helv. Chim. Acta*, 1921, **4**, 505; *A.*, 1921, i, 573; L. Ruzicka, J. Meyer, and M. Mingazzini, *ibid.*, 1922, **5**, 345; *A.*, 1922, i, 560.

[30] L. Ruzicka and F. C. Seidel, *ibid.*, 1922, **5**, 369; *A.*, 1922, i, 562; *Ann. Reports*, 1922, **19**, 118.

[31] L. Ruzicka and M. Stoll, *ibid.*, 1924, **7**, 84; *A.*, i, 302.

Cadinol, the related alcohol, $C_{15}H_{26}O$, which on dehydration gives cadinene, is probably a mixture of two individuals corresponding with the two formulæ for cadinene (the presence of a γ-cadinol is suspected) : [32]


(α-*Cadinol.*)


(β-*Cadinol.*)

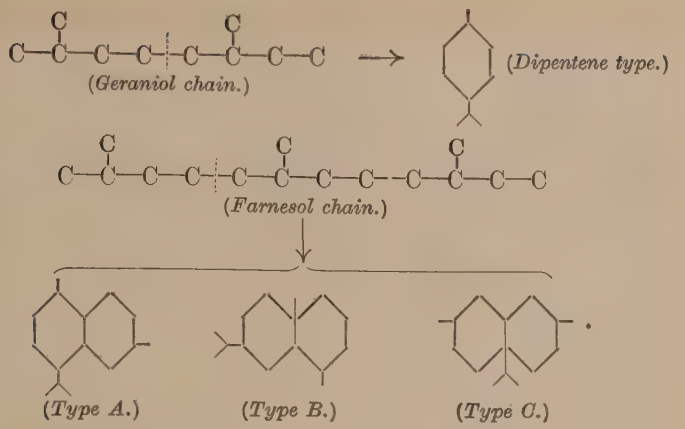
It is not necessary that a sesquiterpene should contain the complete double ring system in order to give a naphthalene derivative on dehydrogenation. Zingiberine, for instance, is a trebly unsaturated monocyclic sesquiterpene with a 5-carbon side chain, which becomes closed during dehydrogenation. Farnesol on dehydration yields a quadruply unsaturated open-chain sesquiterpene, farnesene,[33] which is very similar to a sesquiterpene in Javanese citronella oil. Thus not only dicyclic sesquiterpenes, but also monocyclic and open-chain sesquiterpenes, may be regarded as closely related to the naphthalene hydrocarbon cadalene.

It has been remarked (p. 101) that the farnesol chain, which consists of three isoprene residues joined end to end, can be coiled up to produce the cadinene framework, just as the geraniol chain, composed of two isoprene residues, can be made to give the dipentene skeleton. A hypothesis as to the types of dicyclic sesquiterpene structure likely to be encountered may be formed if it is observed that, whilst the geraniol chain can give only one methyl*iso*propylhydrobenzene, the farnesol chain can yield three (and only three) dimethyl*iso*propylhydronaphthalene nuclei, namely the cadinene skeleton (A) and two others (B and C) : [34]

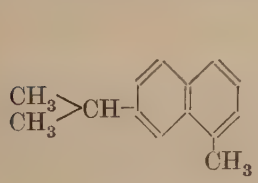
[32] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1924, **7**, 94; *A.*, i, 302.
[33] L. Ruzicka, *ibid.*, 1923, **6**, 492; *A.*, 1923, i, 691.
[34] Types such as

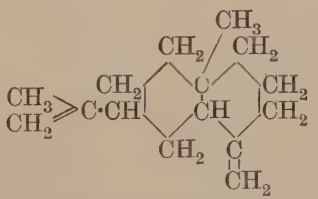
and

appear to be excluded by the rule that, if any alternative is available, the chain will not close in such a way as to have 1 : 1-dialkyl groups attached to an unbridged *cyclo*hexane nucleus (compare C. K. Ingold, *J.*, 1921, **114**, 953). It can easily be seen that this condition necessitates the presence of an *iso*propyl group in any terpene or sesquiterpene structure which does not contain a bridged six-membered ring, and limits the number of types as stated.



It is of great interest, therefore, that although most of the sesquiterpenes and their alcohols that have been examined yield cadalene (Type A) on dehydrogenation, a second series has been discovered, which yields a different naphthalene hydrocarbon, called "eudalene," [35] related to Type B.





The sesquiterpene selinene and the alcohol eudesmol belong to the class which yields eudalene. The position of the double linking in selinene has been determined (principally by ozonolysis), and proof has been given of the position of the methyl group lost in the conversion into eudalene.[36] The precise structure of eudesmol does not yet appear to have been ascertained.

The third group of dicyclic sesquiterpenes to be expected on the above hypothesis, those containing the framework (C), should yield 2 : 7-dimethylnaphthalene on dehydrogenation, but no member of this class has yet been discovered.

It may be added that much work is in progress on the diterpenes. This subject, however, does not yet appear to be in a condition upon which it would be useful to report.

[35] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1922, **5**, 923; *A.*, 1923, [i], 119; *Ann. Reports*, 1923, **20**, 100.

[36] *Idem, ibid.*, 1923, **6**, 864; *A.*, 1923, i, 1216.

The Effect of Position on the Physical Properties of Benzene Derivatives.

It will be of interest to everyone that the researches on the above subject, published since 1915, by Sidgwick and his collaborators have now reached a point at which it has been found possible, not only to co-ordinate the facts, but also to offer a reasoned theory capable of accounting simply for a considerable section of them.[37] The theory is based fundamentally on Werner's theory of co-ordination (and the electronic interpretation thereof), and it makes particular use of the idea of co-ordinated hydrogen. It is probable that the publication of this paper marks a new stage in the correlation of physical properties with constitution, because it brings a new point of view to the aid of that difficult study, to which little imaginative insight has hitherto been applied.

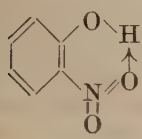
The properties studied were solubility and volatility, and at the outset a clear distinction was drawn between properties possessed by a substance in the solid state—that is, properties largely determined by crystalline forces—and those found in the liquid state, in which the only structural unit is the molecule. It is in the liquid state that we may expect to find the simplest relation between physical constants and structure, and accordingly the whole investigation relates to the liquid state.

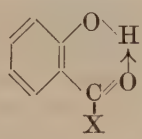
Broadly speaking, benzene derivatives may be divided into "normal" and "abnormal," the term "abnormality" meaning that the isomerides (*o*-, *m*-, and *p*-) differ widely in their volatility and solubility, properties which, in the majority of benzene derivatives, are little influenced by the position of the substituents. The structural conditions necessary for the appearance of abnormality are, (1) that the molecule contain two "active or alterable substituents" (OH, NH_2, CO_2H, CHO, NO_2, Cl, as opposed to "unalterable substituents" such as the alkyls), (2) that of these two groups at least one must be OH, NH_2, substituted NH_2, or CO_2H. The existence of two different panels of groups shows that two functions have to be fulfilled in the production of abnormality: one group makes the compound sensitive, and the other acts on that sensitivity, like the chromophore and auxochrome groups in a dye. The type of variation from the normal depends primarily on the group belonging to the second list, that is, whether the compound is a phenol, an amine, or an acid. These are considered in turn.

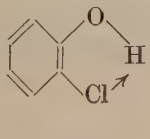
In the case of phenols (containing as a second substituent one of the groups in the first list) the abnormality consists in the fact

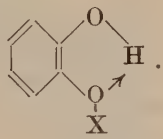
[37] N. V. Sidgwick and R. K. Callow, *J.*, 1924, **125**, 527. References to fourteen earlier papers are given in the original.

that whilst the meta- and para-compounds resemble one another as closely as do normal isomerides, the ortho-compounds differ markedly from them (*a*) in being more volatile, (*b*) in being less miscible with water, (*c*) in being more miscible with benzene. These properties are characteristic of " non-polar " as opposed to " polar " substances, the adjectives being used in a wide sense to distinguish groups of properties characteristic in an especial degree of non-hydroxylic as opposed to hydroxylic compounds. In other words, the ortho-compounds are far less polar than the meta- and para-. The polar characteristic natural to a phenol is, then, suppressed by an " active " group in the ortho-position much as if the hydroxylic hydrogen had been replaced by methyl. The theory advanced is that the hydroxylic hydrogen becomes attached by a co-ordinate linking to some atom of the second group as in formulæ (X)—(XIII), in which an arrow pointing to the hydrogen atom is used for the co-ordinate bond which restrains its polar functions :


(X.)


(XI.)


(XII.)


(XIII.)

Formula (X) depicts the supposed cause of abnormality in the nitrophenols, and formula (XI) that due to the carboxyl, carbethoxyl, and aldehydo-groups. The chelate rings contained in these two formulæ are of the most stable type known—6-membered rings with two conjugated double linkings. In the case of the other active groups (halogens, OH, OAlk, and possibly NH_2), the presence of the rather less stable, five-membered chelate ring must be assumed (formulæ XII and XIII), and accordingly, the abnormality, although present, is in these cases less marked. Chelate compounds always tend to be non-polar (compare the metal acetylacetones), and the ring structure explains why *o*-nitrophenol cannot form compounds with aniline, *p*-toluidine, benzamide, and acetamide, whereas *m*- and *p*-nitrophenols can; and why, if the phenol has active substituents in both *o*- and *p*-positions (*e.g.*, *op*-dinitrophenol), the influence of the ortho-group predominates and the compound is non-polar.

As to the mechanism of the formation of the co-ordinate link and the chelate ring, it is to be noted that the atom to which the hydrogen atom becomes joined is always one which may be assumed to be a seat of residual affinity. In the case of univalent chlorine, bivalent oxygen, or tervalent nitrogen, the corresponding electronic picture is that of an atom which possesses several unshared

electrons in its octet, and is able to use a pair of them as a " bond " to attract the hydrogen nucleus. This is the view adopted by the authors, and the extension of their work on phenols will be awaited with interest, because certain crucial experiments to reveal the mechanism more closely would obviously be possible if the lists of active and inactive groups were longer than they are at present.

The behaviour of the two other main groups, the substituted anilines and substituted benzoic acids, is quite different from that of the phenols, and more complicated—too complicated, perhaps, to be usefully reported on at the present time. Although the data display regularities and have been grouped together, they are not such that the theory of co-ordinated hydrogen can be straightforwardly applied, and no generally applicable theory has yet been advanced.

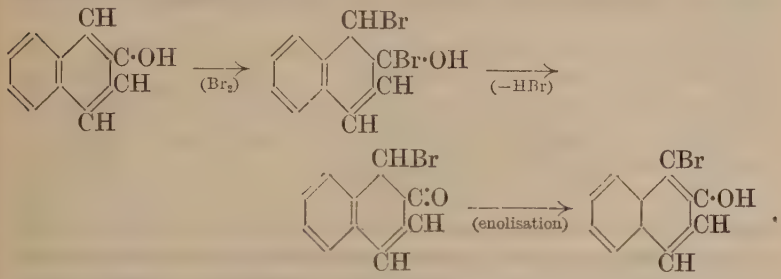
Reactions of Aromatic Compounds.

Ortho- and Para-additions to the Benzene Ring.—The view that the properties of all benzene derivatives could be traced back to purely aliphatic types, if the aliphatic types themselves and the successive stages in the " evolution " of aromatic types from them were better known, is nowhere more simply illustrated than in the case of the phenols, which present perfect analogies with the keto-enol and keto-cyclol types in the aliphatic series. Although Baeyer favoured the centric formula during his earlier researches on benzene structure, he concluded in his final paper (despite the difficulty of understanding, at that time, the diminished unsaturation of the component parts of Kekulé's structure) that certain phenols undoubtedly possessed the Kekulé formula, and, consequently, keto-enol tautomeric character.[38] Further, it has been shown that the general reactions of the phenols, like halogenation and alkylation, as well as peculiarly " aromatic " reactions, such as Tiemann and Reimer's, conform to well-known aliphatic keto-enol and keto-cyclol types.[39] It is of interest to note that in developing his bromine-titration method for estimating enols K. Meyer employed

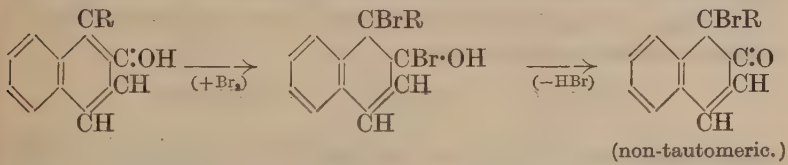
[38] *Annalen*, 1892, **269**, 188; *A.*, 1892, **62**, 1214. The closing remark in which Baeyer epitomises the whole of his experience with the benzene problem, is as incisive to-day as when it was written. " The benzene nucleus," he says, " exists in two forms which may be regarded as tautomeric in the sense that every individual derivative has a definite constitution; this view best explains the facts, and gains enhanced probability when it is considered that the *ortho-* and *para*-linking in phenanthrene and anthracene, respectively, have almost identical properties and are similar to the ' breakable ' linkings in the molecule of benzene."

[39] C. K. Ingold, *J.*, 1922, **122**, 1133; compare also W. Fuchs and B. Elsner, *Ber.*, 1924, **57**, [*B*], 1225; *A.*, i, 960.

β-naphthol as a typical enol to take up the excess of bromine. According to his general theory of the mechanism, the first step must be 1 : 2-addition to the Kekulé double linking, and a bromoketone must intervene :

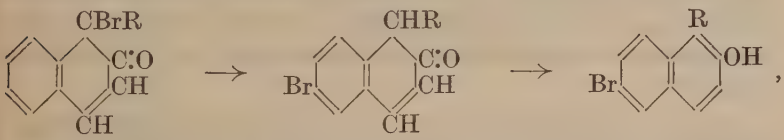


Now, just as in the case of the Tiemann-Reimer reaction, it should be possible to obtain evidence of the correctness of the above mechanism by the introduction of a "blocking group," which, by preventing the final tautomeric change, would arrest the chain of reactions at an earlier stage and thus reveal the mechanism :



(non-tautomeric.)

This has now been done, and a considerable number of bromoketones of the type indicated have been isolated.[40] Although they cannot enolise, they can isomerise, in the presence of hydrogen bromide, to 6-bromo-β-naphthols :



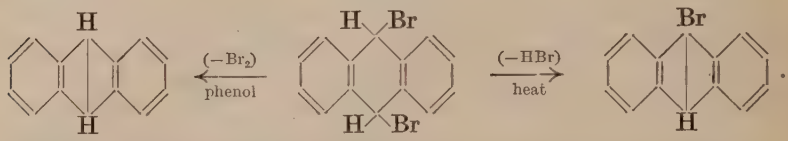
a reaction which, if account is taken of the para-affinity in the benzene ring, is an ordinary αγ-migration, promoted by the loosening influence of the adjacent carbonyl group on the bromine atom. It is strictly analogous to the well-known conversion, also in the presence of hydrogen bromide, of ethyl α-bromoacetoacetate into ethyl γ-bromoacetoacetate.[41]

The para-addition of bromine to the *meso*-ring of anthracene

[40] K. Fries and H. Engel, *Annalen*, 1924, **439**, 232; *A.*, i, 1187.

[41] A. Hantzsch, *Ber.*, 1894, **27**, 356, 3168; *A.*, 1895, i, 81; M. Conrad, *Ber.*, 1896, **29**, 1040; *A.*, 1896, i, 409.

has been shown to be reversible, since, on the addition of a substance, such as phenol, capable of combining easily with free bromine, anthracene is regenerated. On heating in the absence of a bromine-remover, however, not bromine but hydrogen bromide is eliminated; [42]



Similarly, the re-establishment of para-affinity in the intermediate 9 : 10-additive compound obtained on nitrating 9-bromoanthracene may take place in two ways, eliminating either water, giving 9-bromo-10-nitroanthracene, or hydrogen bromide, yielding 9-hydroxy-10-nitroanthracene. Actually there is evidence of the occurrence of both reactions,[43] although the hydroxy-nitro-compound at once changes into the anthrone, an instance of the keto-cyclol tautomeric change first investigated in detail by K. Meyer.[44]

Addition to Unsaturated Side-chains.—The hypothesis that all additive reactions of the type :

$$[H]—C + X=Y = C—X—Y[H]$$

are reversible and hence may be employed to assist the understanding of the triad tautomeric changes of which they are the intermolecular prototypes [45] appears to be turning out correctly. It was previously rendered probable by the proof that equilibria arise in the aldol [46] and Michael [47] additive reactions, and has now been further confirmed by an investigation of the cyano-imino-additive process elaborated by Thorpe and his co-workers. The establishment of equilibrium was ascertained in the following cases : [48]

$$C_6H_5\cdot C{:}N + CH[H](CN)\cdot CO_2Et \rightleftharpoons C_6H_5\cdot C(:N[H])\cdot CH(CN)\cdot CO_2Et.$$
$$C_7H_7\cdot C{:}N + CH[H]Ph\cdot CN \rightleftharpoons C_7H_7\cdot C(:N[H])\cdot CHPh\cdot CN.$$

Knoevenagel's method of producing cinnamic acids by treating aromatic aldehydes with aniline and malonic acid evidently depends

[42] E. de B. Barnett and J. W. Cook, *J.*, 1924, **125**, 1084.
[43] *Idem, ibid.*
[44] *Annalen*, 1911, **379**, 37; *A.*, 1911, i, 193.
[45] E. H. Usherwood, *Chem. and Ind.*, 1923, **42**, 1246; *A.*, 1924, i, 139; *J.*, 1923, **123**, 1717.
[46] *Idem, ibid.*
[47] C. K. Ingold and W. J. Powell, *J.*, 1921, **119**, 1977.
[48] E. H. Ingold (Usherwood), *J.*, 1924, **125**, 1313.

on the reversibility of two additive processes with a common addition product :

$$C_6H_5\cdot CH{:}NPh + CH_2(CO_2H)_2 \rightleftharpoons C_6H_5\cdot CH{<}\begin{matrix}NHPh\\CH(CO_2H)_2\end{matrix} \rightleftharpoons C_6H_5\cdot CH{:}C(CO_2H)_2 + NH_2Ph$$

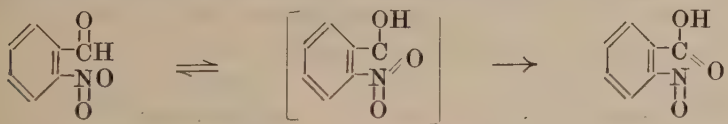
for the reaction is known to take place just as well (or better) when the pure anil is employed instead of a mixture of the aldehyde and aniline, and, in the latter case, as K. W. Rosenmund and T. Boehm have shown,[49] the formation of an anil is a necessary antecedent condition. Those aldehydes, like gallaldehyde, the initial addition products of which with aniline [of the type R·CH(OH)·NHPh] are too stable to lose water and give an azomethine under the conditions employed, cannot be converted into cinnamic acids by this method.

The peculiar properties of aromatic aldehydes have frequently been commented upon, especially their ready oxidation by air, which, it has been suggested, involves a tautomeric change of the dyad type into a modification possessing much greater additive power : [50]

$$CHPh{:}O \rightleftharpoons \begin{matrix}Ph\\HO\end{matrix}{>}C \xrightarrow[(+O_2)]{} \begin{matrix}Ph\\HO\end{matrix}{>}C{:}O{:}O$$

$$\begin{matrix}Ph\\HO\end{matrix}{>}C{:}O{:}O + C{<}\begin{matrix}Ph\\OH\end{matrix} \longrightarrow 2\begin{matrix}Ph\\HO\end{matrix}{>}C{:}O$$

Whether this can be confirmed or not, it is practically certain that a peroxide intervenes as the scheme requires. The aldehyde group can also be oxidised by an internal process, as is shown by the fact that *o*-nitrobenzaldehyde, when exposed to light in an indifferent solvent, passes into *o*-nitrosobenzoic acid : [51]



M. Passerini's remarkable observation [52] that the anils of certain aromatic aldehydes add on to carbylamines may perhaps be accounted for in the same way :

$$CHR{:}NPh \rightleftharpoons \begin{matrix}R\\NHPh\end{matrix}{>}C \xrightarrow[(C{:}NPh)]{} \begin{matrix}R\\NHPh\end{matrix}{>}C{:}C{:}NPh \longrightarrow \begin{matrix}R\\NPh\end{matrix}{>}C\cdot CH{:}NPh,$$

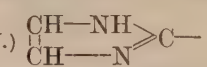
[49] *Annalen*, 1924, **437**, 125; *A.*, i, 733.
[50] E. H. Ingold (Usherwood), *J.*, 1924, **125**, 1530.
[51] G. Heller, *J. pr. Chem.*, 1923, [ii], **106**, 1; *A.*, 1924, i, 736.
[52] *Gazzetta*, 1924, **54**, 667; *A.*, **i**, 1319.

but the theory of addition without previous isomeric change, although, perhaps, improbable on general grounds, cannot be excluded on the evidence available.

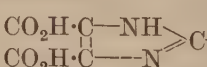
Orientation.—In view of the multiplicity of substitution rules, a determination of the directive action of a group not previously investigated in this connexion assumes considerable importance. The directive effect of the thiocyano-group (·S·C⋮N) was previously unknown, and it is of interest to record that F. Challenger and A. D. Collins have found it to be ortho-para-directing, the tendency being towards para-substitution when other groups are absent.[53] The authors note the fact that the observed directive influence is in agreement with the theory of alternate polarities, but do not state what is equally relevant, namely, that the same facts (like most of the data on directive influence at present available) agree just as well with Flürscheim's principle of alternating affinity distribution, the essential validity of which, and its general ability to account for directive effects, are everywhere admitted. The only assumption that the known data on directive influence appear really to justify is that *some* kind of an alternating property exists. As to its nature, two theories have been advanced, and the new results are equally favourable to both.

It seems desirable to point this out, because the experiments referred to are not the only ones which have been presented with reference to the polarity theory, although capable of more than one interpretation.*

Another interesting case is that recorded by F. L. Pyman and E. Stanley. In the nitration of 2-phenylglyoxaline, the glyoxaline residue (XIV) directs mainly towards the para- and ortho-positions of the phenyl group, whereas in the nitration of the 4 : 5-dicarboxy-derivative, the residue (XV) produces the opposite effect, the principal product being the *m*-nitro-compound : [54]

(XIV.) 

(*mainly* o-p-*directing.*)

 (XV.)

(*mainly* m-*directing.*)

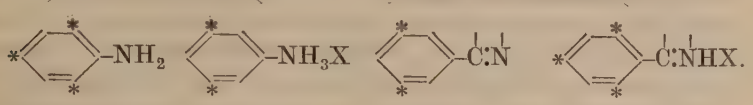
The difference between the two cases appears to be connected with the fact that the phenylglyoxaline yields salts with mineral acids, whilst its dicarboxylic acid does not, so that in the first case the substance nitrated is not the phenylglyoxaline itself but its nitrate. On this view, the key to the orienting influence is the

[53] *J.*, 1924, **125**, 1377.

* In such cases, would it not be better to keep phraseology within the boundaries of ascertained fact,—or, at least, generally agreed deduction,—and speak of results as supporting "the alternating principle"?

[54] *J.*, 1924, **125**, 2484.

condition, as regards salt formation, of the doubly-bound nitrogen atom, and the observed difference may be compared with that between the directive effects of $-NH_2$ and of $-NH_3X$:—



(*ortho-para.*) (*meta.*) (*meta.*) (*ortho-para.*)

The reversal of the effect on removing the nitrogen atom one place further from the benzene nucleus, both in the case of the bases themselves and their salts, is a particularly clear indication of the alternating character of the influence transmitted, but, as the authors observe, it is equally in accordance with both theories as to the character of that influence.

The Isomerism of the Oximes.—The history of oxime chemistry has recently passed through a phase which seems like an echo of the events of 1889—1890.[55] In 1921, F. W. Atack and L. Whinyates [56] reported the discovery of a fourth dioxime of benzil, and, partly on the strength of this, Atack [57] levelled a strong criticism against Hantzsch and Werner's stereochemical hypothesis. This it was proposed to discard, and replace by a purely structural theory, by which, it was claimed, the isomerism and properties of oximes could be completely explained without resort to spatial suppositions. The theory proposed embodied that of Beckmann, who first suggested the "oxime" and "*iso*oxime" formulæ, $RR'C{:}NOH$ and $RR'C\overset{O}{\diagdown}\!\!-\!\!NH$, for the isomeric oximes usually termed "anti" and "syn" respectively; but the new theory postulated in addition a third unstable structure, $RR'C{:}N\overset{O}{\diagdown}\!\!-\!\!H$, to which the name "nitrone" was given. It is clear that, according to this theory, there should be six benzildioximes, whereas the stereochemical hypothesis requires the existence of only three. It was also suggested that the latter theory could not account for the differences in the reactivity of the aldoximes, that it afforded no precise mechanism for their interconversion, and that it led

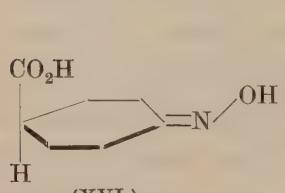
[55] K. Auwers and V. Meyer, *Ber.*, 1889, **22**, 537, 565, 705; *A.*, 1889, i, 607, 611, 713; *idem, ibid.*, 1890, **23**, 2403; *A.*, 1890, i, 1268; E. Beckmann, *ibid.*, 1889, **22**, 429, 514, 1531, 1588; *A.*, 1889, i, 607, 608, 979, 980; K. Auwers and M. Dittrich, *ibid.*, p. 1996; *A.*, 1889, i, 1192; H. Goldschmidt, *ibid.*, p. 3109; *A.*, 1890, i, 251; *idem, ibid.*, 1890, **23**, 2163; *A.*, i, 1890, i, 1261; A. Hantzsch and A. Werner, *ibid.*, p. 11; *A.*, 1890, i, 348. Compare Lachman, "The Spirit of Organic Chemistry," Chapter VIII.

[56] *J.*, 1921, **119**, 1184.

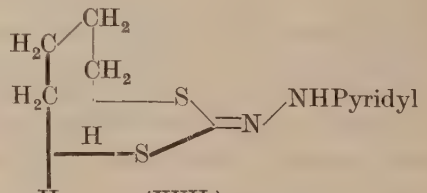
[57] F. W. Atack, *ibid.*, p. 1175.

to discrepancies when the configurations assigned on the basis of the Beckmann change could be checked, as in the case of the benzildioximes, by independent evidence relating to the properties of the oximes themselves.

It is obvious that, although much of this indictment is true, a great deal still remains to be said on the whole question. Leaving, for the moment, the specific objections to the stereochemical theory, it may be noted that there are three strong reasons for retaining it. (1) No purely structural theory can account for the failure to obtain more than one oxime in the case of symmetrical ketones. This point, although touched upon by Atack, is very inadequately dealt with. (2) The stereochemical theory is the only one which accounts for the production of two isomeric *O*-ethers. The existence of isomeric *O*-ethers was doubted by Atack, but, as O. L. Brady and F. P. Dunn have pointed out,[58] the evidence in favour of their existence is overwhelming, and cannot be neglected. (3) W. H. Mills and A. M. Bains's proof [59] of the Hantzsch-Werner hypothesis by the preparation of the optically active "centro-asymmetric" oxime (XVI) is apparently quite conclusive. Atack's suggestion that the optical activity observed by Mills and Bains might be due to the occurrence of the "nitrone" form cannot now be upheld, since Mills and H. Schindler [60] have obtained an optically active centro-asymmetric hydrazone (XVII),—clear proof that Hantzsch and Werner's fundamental postulate relates essentially to doubly-bound tervalent nitrogen.



(XVI.)



(XVII.)

But although the solution of the oxime problem cannot be obtained by the *rejection* of the stereochemical conception, the necessity for its *extension* is plain, and it is by directing attention to this fact that Atack's critical review has been of service. At an early date, however, Hantzsch and Werner were aware that structural isomerism could not be excluded, and both of them adopted the *iso*oxime structure as the best expression for the *N*-ethers of the oximes.[61] Their view has since been generally

[58] *J.*, 1924, **125**, 291.
[59] *Ibid.*, 1910, **97**, 1866.
[60] *Ibid.*, 1923, **123**, 312.
[61] A. Hantzsch, "Grundriss der Stereochemie," 1904, p. 120; A. Werner, "Lehrbuch der Stereochemie," 1904, p. 235.

accepted, but a considerable body of evidence has been amassed [62] in favour of the nitrone structure for the same series of compounds. This, perhaps, is to be expected, as the *iso*oxime and nitrone formulæ are very intimately related (they are mere valency-isomerides), and therefore much more likely to represent phases of an extremely mobile tautomeric system than individuals capable of separate existence :

$$RR'C{=}NX \rightleftharpoons RR'C\!-\!NX \quad (X = H, \text{ alkyl, etc.}).$$
$$\qquad\quad \| \qquad\qquad\quad \diagdown\diagup$$
$$\qquad\quad O \qquad\qquad\quad O$$

Since definite individuals of this type (*iso*oxime, or nitrone, or both) can be isolated in the case of the alkyl derivatives of the oximes, the same type of structure may be expected to occur amongst the oximes themselves, at least as relatively unstable tautomeric forms.[63]

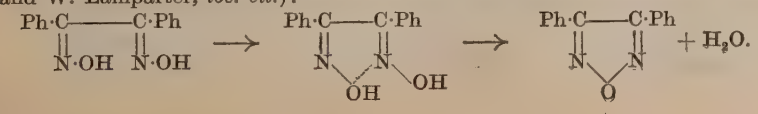
It follows that although the stereochemical theory does not supply a ready-made explanation of the isomeric changes and reactivities of oximes, the theory, when extended on lines foreshadowed by Hantzsch and Werner, leaves plenty of scope for an interpretation of these phenomena. As to Atack's other criticisms, doubt has been cast [64] on the existence of the fourth benzildioxime, and even if it does exist, the fact would not invalidate the stereochemical hypothesis, since the hypothetical *iso*- or nitrone-form might in certain cases be sufficiently stable to have a separate existence (compare p. 114). With regard to the discrepancies relating to the Beckmann rearrangement, the main obscurity here is the mechanism of the change itself, and this question is at present being studied by Meisenheimer and his collaborators.[65]

[62] M. O. Forster and H. Holmes, *J.*, 1908, **93**, 244; A. Angeli, L. Alessandri, and M. Aiazzi-Muncini, *Atti R. Accad. Lincei*, 1911, [v], **20**, i, 546; *A.*, 1911, i, 544; O. L. Brady, *J.*, 1914, **105**, 2104; H. Staudinger, K. Miescher, and E. Schlenker, *Helv. Chim. Acta*, 1919, **2**, 554; *A.*, 1919, i, 584; K. von Auwers and B. Ottens, *Ber.*, 1924, **57**, [*B*], 446; *A.*, i, 516.

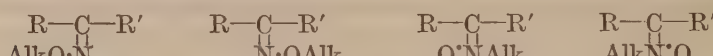
[63] O. L. Brady and F. P. Dunn, *J.*, 1916, **109**, 659.

[64] *Idem*, *ibid.*, 1924, **125**, 291; J. Meisenheimer and W. Lamparter, *Ber.*, 1924, **54**, [*B*], 276; *A.*, i, 432.

[65] J. Meisenheimer, *Ber.*, 1921, **54**, [*B*], 3206; *A.*, 1922, i, 152; J. Meisenheimer and W. Lamparter, *loc. cit.*; J. Meisenheimer and H. Lange, *ibid.*, p. 282; *A.*, i, 433; J. Meisenheimer and H. Meis, *ibid.*, p. 289; *A.*, i, 433. The mechanism of the Beckmann rearrangement need not be discussed here, as, whatever may be the solution, it can scarcely affect oxime theory, excepting, possibly, to alter the allocation of configurations amongst groups of stereoisomerides. It should be noted, however, that the great tendency possessed by *amphi*-benzildioxime, the configuration of which is not in doubt, to pass into an anhydride seems to necessitate a new conception of the mechanism of anhydride formation amongst oximes (J. Meisenhemer and W. Lamparter, *loc. cit.*):



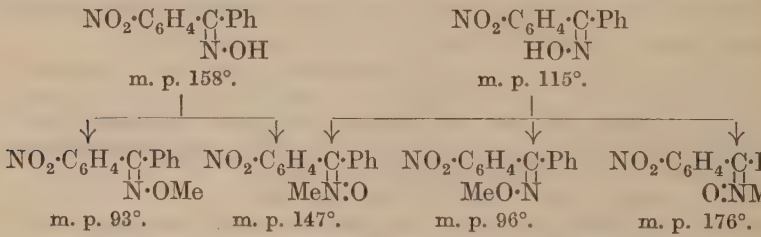
Opinion appears, then, to be once more united on the subject of the existence of stereoisomeric oximes of the type RR′C:NOH, and it is now asked whether the *iso-* and nitrone-structures may also have definite stereochemical configurations capable of leading to isomerism amongst the *N*-ethers of the oximes. The first answer to this question came in 1918, when L. Semper and L. Lichtenstadt [66] obtained two crystalline *N*-methyl ethers of phenyl *p*-tolyl ketoxime, and also two *O*-ethers, one of which, however, was an oil and of doubtful purity. Recently, however, two complete series of two crystalline *N*-ethers and two crystalline *O*-ethers have been described. Using the nitrone formula for the *N*-ethers, the isomerides may be formulated as follows :



The first series was obtained by A. Plowman and M. A. Whiteley [67] from the mesoxmono-*p*-tolylamide oximes,

$$NH_2\cdot CO\cdot C(:NOH)\cdot CO\cdot NH\cdot C_7H_7,$$

which will be referred to again below, and the second by O. L. Brady and R. P. Mehta [68] from the oximes of *p*-nitrobenzophenone. In the latter case, the configurations of the ethers follow clearly from those of the parent oximes, which were oriented by the Beckmann rearrangement, adopting the convention of *cis*-interchange of radicals :



It seems plain from these results that the stereochemical theory of Hantzsch and Werner requires substantial extension, if it is to be applied to all the ethers of the oximes; but the investigation of Plowman and Whiteley [69] raises the further point as to whether it may not be possible to isolate the parent *iso*oximes themselves, and to obtain them, moreover, in *syn-* and *anti*-modifications; for the four ethers described by these investigators were derived from no fewer than five forms of the free oxime. It is suggested that these varieties include, not only the *syn-* and *anti*-modifications of the *iso*oxime proper (*i.e.*, the ring form as distinct from the

[66] *Ber.*, 1918, **51**, 928; *A.*, 1918, i, 437.
[67] *J.*, 1924, **125**, 587.
[68] *Ibid.*, p. 2297.
[69] *Loc. cit.*

nitrone form), but also a true nitrone, in addition to the *syn-* and *anti*-forms of the normal oxime. This is a very interesting possibility, but as Brady and Mehta [70] point out, caution must be exercised in assigning definite structures to these compounds, as the presence of the carbonyl groups, with consequent opportunities for tautomerism, introduces a certain ambiguity.

Free Radicals. Tervalent Carbon, Bivalent Nitrogen, and Univalent Oxygen.

Tervalent Carbon.—The position with regard to the triphenylmethyl problem reached in 1910 as a result of Schmidlin and Schlenk's classical experiments has now been thoroughly upset, and the simple scheme [71]

$$\underset{\text{(colourless, non-oxidisable)}}{Ph_3C{-}CPh_3} \rightleftharpoons \underset{\text{(coloured, oxidisable)}}{2Ph_3C{-}} \quad . \quad . \quad . \quad (A)$$

at one time regarded as established, requires additions if not actual modifications.

In order to understand the extent to which the various complicating influences affect the elementary conception, it is necessary to draw a clear distinction between "thermal" and electrolytic dissociation. When solid hexaphenylethane is dissolved in a non-dissociating solvent such as benzene, there is no doubt that "thermal" dissociation into the radical (equation A) is the principal reaction. If, however, a dissociating solvent, such as sulphur dioxide, is used, the solution obtained conducts electricity, and therefore, presumably, contains ions in place of, or in addition to, the radical (equation B): [72]

$$Ph_3C{-}CPh_3 \rightleftharpoons Ph_3C^{\oplus} + Ph_3C^{\ominus} \quad . \quad . \quad . \quad (B)$$

Now these three triphenylmethyls, the two kinds of ions and the radical, will differ from one another in their physical and chemical properties as completely, perhaps, as atomic iodine does from the iodide ion. To take the most obvious characteristic—colour—it is not surprising that the absorption spectrum of triphenylmethyl in sulphur dioxide or hydrogen cyanide is totally different from that in non-dissociating solvents like benzene, and that with other triarylmethyls the differences are obvious to the unaided eye.[73] The chemistry of triphenylmethyl is, therefore, in the first instance, that of three distinct individuals, and too great emphasis cannot be laid on this point, as much confusion has been caused by attempts to combine

[70] *Loc. cit.*

[71] B. Flürscheim, *J. pr. Chem.*, 1905, [ii], **71**, 505; *A.*, 1905, i, 614.

[72] Solvation is neglected in the formulæ.

[73] M. Gomberg and F. W. Sullivan, *J. Amer. Chem. Soc.*, 1922, **44**, 1829.

conclusions reached by different methods, without regard to the conditions under which the various experimental observations were made.

The positive and the negative ions cannot conveniently be studied separately in solutions of triphenylmethyl itself, but the positive ions can be obtained without their negative isomerides in solutions of triphenylmethyl chloride, and probably the negative ions without the positive ones could be found in solutions of sodium triphenylmethyl if a suitable dissociating solvent were known :

$$Ph_3CCl \rightleftharpoons Ph_3C^{\oplus} + Cl^{\ominus}$$
$$Ph_3CNa \rightleftharpoons Ph_3C^{\ominus} + Na^{\oplus}$$

The positive ion produced from the halide has in fact been studied in great detail by Gomberg and his collaborators, who have shown that it is in equilibrium with a tautomeric quinonoid form :

The negative ion has not yet been closely studied, but it is of great interest that C. A. Kraus and T. Kawamura [74] have evolved an improved method of producing the metallic compounds, and have even obtained an ammonium derivative, although this is unstable and soon decomposes into triphenylmethane and ammonia :

$$CPh_3Na;\ CPh_3K;\ CPh_3{\cdot}NH_4 \longrightarrow CPh_3H + NH_3.$$

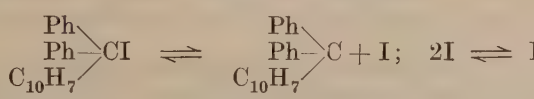
The sodium, potassium and ammonium derivatives are all red solids, the potassium compound being stable even at 100°. The metallic compounds are obtained by the action of the metals on triphenylmethyl chloride in liquid ammonia, and the ammonium derivative by the action of ammonium chloride in liquid ammonia on the sodium compound. The instantaneous character of this double decomposition strongly suggests the ionisation of these compounds in liquid ammonia solution. It is possible that substituted ammonium derivatives may be obtained by similar methods, and may prove more stable than the ammonium compound itself, and have solubilities suitable for the investigation of the negative triphenylmethyl ion in a dissociating solvent.

As regards the uncharged radical, it has been suggested [75] that this undergoes tautomeric change similar to that which was proved to occur in the case of the positive ion :

[74] *J. Amer. Chem. Soc.*, 1923, **45**, 2756; *A.*, 1924, i, 276.
[75] M. Gomberg, *Ber.*, 1913, **46**, 228.

However, the evidence on which this supposition is based is by no means clear, for, as we have seen, the results of experiments involving the ion have no bearing in this case. It has been proved,[76] using diphenyl-β-naphthylmethyl in various non-dissociating solvents, that the apparent molecular weight diminishes, as it should, with rise of temperature and with dilution, but that the depth of colour increases faster than the dissociation for a rise of temperature, and in some solvents faster, and in others slower, than the dissociation on dilution. Further, the proportion of material immediately oxidisable with air, with loss of colour, is always less than the proportion dissociated. But it is very difficult to explain these facts by the tautomeric hypothesis alone, and it is by no means clear that they could not adequately be accounted for by the formation, with the solvent employed, of loose molecular compounds, such as the triarylmethyls are known to have a strong tendency to produce.

The question as to whether the triarylmethyl halides break up in electrolytically non-dissociating solvents to give the radical, just as they do in dissociating solvents to give the ion, has been answered in the affirmative, because the equilibrium between diphenyl-β-naphthylmethyl iodide, the free radical, and iodine has been found to be of a measurable order : [77]



From this point of view, the numerous reactions of the triarylmethyl halides in which the halogen parts from the methane carbon atom take on an enhanced interest ; [78] as also perhaps do the reactions of acid halides, which the triarylmethyls closely resemble.[79]

The tendency possessed by the triarylcarbinols to divide, in addition reactions, thus : R_3C-OH, as well as in the way usual amongst alcohols, namely, $R_3C\cdot O-H$, is well illustrated by some experiments of D. R. Boyd and F. J. Smith [80] on the interaction between triphenylcarbinol and phosphorus trichloride. The reaction proceeds according to equation (C) to the extent of 78% of the carbinol employed (the normal reaction between phosphorus

[76] M. Gomberg and F. W. Sullivan, *loc. cit.*, p. 1810; *A.*, 1922, i, 929.

[77] *Idem, ibid.*

[78] Compare J. B. Conant and A. W. Sloan's new method for the preparation of free radicals by reduction of the chlorides with vanadous chloride (*J. Amer. Chem. Soc.*, 1923, **45**, 2466; *A.*, 1924, i, 304).

[79] J. F. Norris, *Ind. Eng. Chem.*, 1924, **16**, 184; *A.*, i, 381; E. Benary and P. Lorth, *Ber.*, 1924, **57**, [*B*], 1324; *A.*, i, 1192; F. F. Blicke, *J. Amer. Chem. Soc.*, 1924, **46**, 1515; *A.*, i, 845.

[80] *J.*, 1924, **125**, 477.

trichloride and an alcohol: Menschutkin, 1866); whilst about 5% of the carbinol reacts in accordance with equation (D):

$$R{\cdot}O{-}H + PCl_3 \longrightarrow \begin{matrix} R{\cdot}O \\ H \end{matrix}\!>\!PCl_3 \xrightarrow{-HCl} R{\cdot}O{\cdot}PCl_2 \quad . \quad . \quad (C)$$

$$R{-}O{\cdot}H + PCl_3 \longrightarrow \begin{matrix} R \\ OH \end{matrix}\!>\!PCl_3 \xrightarrow{-HCl} R{\cdot}\underset{\underset{O}{\|}}{P}Cl_2 \quad . \quad . \quad . \quad (D)$$

It has often been asked whether it is the "affinity-demand" or the "space-demand" of the aryl residues which is responsible for the dissociation of hexa-substituted ethanes. Schlenk's discovery [81] that the *p*-diphenyl group has a greater dissociating influence than phenyl *appears* to favour the view that "affinity-demand," and the consequent alternation in the affinity content of bonds, is the true cause. The same view is strongly advocated by Zeigler,[82] who has found that the introduction of a *gem*-diphenylvinyl residue in place of phenyl also greatly enhances the dissociation:

(*Enhanced dissociation.*)

(*Enhanced dissociation.*)

However, if this were the only factor to be considered, the replacement of phenyl by triphenylmethyl should lead to diminished dissociation:

(*Diminished dissociation.*)

whereas, actually, W. Schlenk and H. Mark [83] proved that a greatly increased dissociation is observed. It is plain, therefore, that the spatial factor is of importance, and that the controlling conditions are somewhat complex. The apparent superposition of "quantitative" and "steric" factors arouses the suspicion that the whole of these dissociation phenomena may be capable of an approximate analysis, similar to that to which B. Flürscheim [84] submitted the

[81] W. Schlenk, T. Weickel, and A. Herzenstein, *Annalen*, 1910, **372**, 1; *A.*, 1910, i, 236.

[82] K. Zeigler, *ibid.*, 1923, **434**, 34; *A.*, 1924, i, 308. Compare also K. Zeigler and B. Schnell, *ibid.*, 1924, **437**, 227; *A.*, i, 850.

[83] *Ber.*, 1922, **55**, [*B*], 2285, 2299; *A.*, 1922, i, 1002.

[84] *J.*, 1909, **95**, 718; 1910, **97**, 84.

available data regarding the electrolytic dissociation of organic acids and bases.

Bivalent Nitrogen.—Evidence of the ability of tetra-arylhydrazines to dissociate giving a coloured and highly reactive radical

$$Ar_2N—NAr_2 \rightleftharpoons 2Ar_2N—$$

was first advanced by Wieland [85] in 1911. Tetraphenylhydrazine, although colourless in the solid state and in solution in the cold, gave a green solution in boiling toluene, in which the presence of the radical could be shown by chemical means (combination with —N:O to form $Ph_2N{\cdot}N{:}O$),[86] although the quantity present in equilibrium with the hydrazine could not be estimated. Greater dissociation was obtained, later (1912), in the case of tetra-anisylhydrazine, and still greater in the case of tetra-(*p*-dimethylaminophenyl)-hydrazine (1915). The increasing dissociation when the para-hydrogen of each phenyl group is replaced first by bivalent oxygen (OMe) and then by tervalent nitrogen (NMe_2) is in good accord with the Werner-Flürscheim theory of affinity-demand :

$$\begin{matrix} H—C_6H_4 \\ H—C_6H_4 \end{matrix}\!\!>\!N— \qquad \begin{matrix} MeO—C_6H_4 \\ MeO—C_6H_4 \end{matrix}\!\!>\!N\text{----} \qquad \begin{matrix} Me_2N—C_6H_4 \\ Me_2N—C_6H_4 \end{matrix}\!\!>\!N\cdots$$

A comprehensive set of cases has been worked out by S. Goldschmidt [87] in the series of hexa-substituted tetrazanes :

$$NR_2{\cdot}NR—NR{\cdot}NR_2 \rightleftharpoons 2NR_2{\cdot}NR—.$$

Hexaphenyltetrazane, for example, gives dark blue solutions, the colour deepening on warming and increasing relatively on dilution. The presence of the triphenylhydrazyl radical, $NPh_2{\cdot}NPh—$, is shown by the formation of the compound $NPh_2{\cdot}NPh{\cdot}NO$ with nitric oxide, and by the instantaneous reduction by quinol to triphenylhydrazine, $NPh_2{\cdot}NPhH$.

As might be expected from the more complex nature of the radical, the relative dissociating influence of different substituents reveals more complex effects than are observed in the triarylmethyls or the diarylnitrogens. Diphenylpicrylhydrazyl is a singular substance. It is definitely monomolecular, even in the solid state, crystallising in black-violet prisms, which look like potassium permanganate. Quinol instantly reduces it to the hydrazine, and the

[85] H. Wieland and H. Lecher, *Annalen*, 1911, **381**, 200; *A.*, 1911, i, 569; *Ber.*, 1912, **45**, 2600; *A.*, 1912, i, 907; *ibid.*, 1915, **48**, 1078; *A.*, 1915, i, 848.

[86] It is noteworthy that this reaction was shown to be reversible like the union of triarylmethyls with iodine.

[87] *Annalen*, 1924, **437**, 194; *A.*, i, 884; see also *Ber.*, 1920, **53**, [*B*], 44; *A.*, 1920, i, 257; S. Goldschmidt and K. Euler, *Ber.*, 1922, **55**, [*B*], 616; *A.*, 1922, i, 475.

change of colour is so marked that the radical can readily be estimated by titration with quinol.

The diacyltetra-aryltetrazanes also are markedly dissociated, but somewhat less so, on the whole, than the hexa-aryl derivatives :

$$NAr(CO\cdot R)\cdot NAr—NAr\cdot NAr(CO\cdot R) \rightleftharpoons 2NAr(CO\cdot R)\cdot NAr—$$

By considering a series of related compounds, the superposition of a spatial and a quantitative, and possibly also a polar, influence may be perceived, although no regular connexion with the strength of the acid corresponding with the acyl group can be discovered. The following " order of dissociation " is illustrative of the facts that have been accumulated : diacetyltetraphenyl < dibenzoyltetraphenyl < diacetyltetratolyl < dibenzoyltetratolyl < diacetyltetra(*p*-dimethylaminophenyl); the last member of the series being almost completely dissociated under ordinary conditions.

It is of interest that, as with triarylmethyls and their corresponding ethanes, the equilibration of the hydrazyls and their tetrazanes is a definite and measurable time reaction. This circumstance, and the fact that the radicals are instantaneously reduced by quinol, have enabled Schmidlin's classical experiment with triphenylmethyl to be paralleled in the case of the hydrazyls. Titration with quinol to complete decoloration indicates the fraction of tetrazane originally dissociated; soon, however, the red colour returns, and the solution then becomes able to react instantaneously with a further quantity of quinol. The only essential distinction from Schmidlin's experiment is that whereas he destroyed his dissociated material by oxidation, Goldschmidt employed reduction.

In view of the puzzling discrepancies noticed by Gomberg and Sullivan (p. 117) when following quantitatively the effect of dilution on the dissociation of hexa-arylethanes, it is reassuring to notice that the tetrazanes dissociate strictly in accordance with Ostwald's dilution law, and that the results can be confirmed colorimetrically. This may, perhaps, be taken as an indication that Gomberg and Sullivan's discrepancies are due to some extraneous influence, and are not likely fundamentally to alter the conception of free radicals.

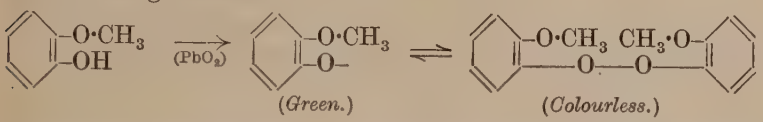
Univalent Oxygen.—In 1914, Wieland [88] prepared diphenylnitric oxide, which may be formulated as containing either quadrivalent nitrogen or univalent oxygen :

$$\begin{matrix}Ph\\Ph\end{matrix}\!\!>\!\overset{\downarrow}{N}\!:O \qquad \text{or} \qquad \begin{matrix}Ph\\Ph\end{matrix}\!\!>\!N—\overset{\downarrow}{O}\,.$$

A more definite example of a free radical containing univalent oxygen was obtained, in 1922, by S. Goldschmidt, [89] who found that

[88] H. Wieland and M. Offenbächer, *Ber.*, 1914, **47**, 2111; *A.*, 1914, i, 955.
[89] *Ibid.*, 1922, **55**, [*B*], 3194; *A.*, 1922, i, 1148.

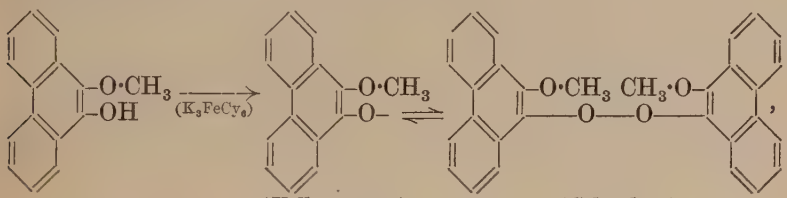
guaiacol, on oxidation with lead peroxide, gave a green solution which was immediately decolorised by quinol or by triphenylmethyl. The suggestion advanced to account for these facts is conveyed by the following formulæ :



(*Green.*) (*Colourless.*)

but neither the green nor the colourless compound could be isolated.

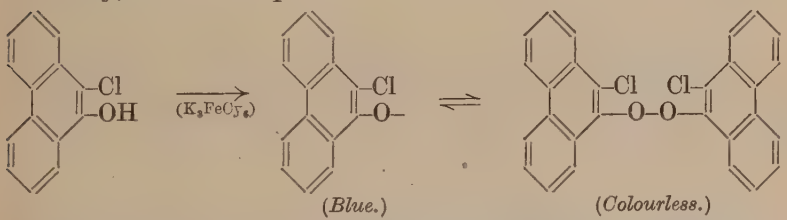
Better fortune has, however, attended more recent investigations [90] in the phenanthrene series. In the case :



(*Yellow-green.*) (*Colourless.*)

the colourless compound was isolated. Its yellow-green solution gave figures for the molecular weight indicating 37% dissociation, and in an analogous example with OEt in place of OMe there was 62% dissociation.

Finally, in the example :



(*Blue.*) (*Colourless.*)

both the colourless and the blue compounds were isolated, and dissociation to the extent of 69% was observed in an equilibrated solution.[91]

In every case the free radical was instantly reduced by quinol or hydrazobenzene, and it combined with triphenylmethyl; both reactions, of course, involve loss of colour. A remarkable point was the slowness with which equilibrium was reached, several hours being usually required in cold solution; it is this fact which enabled both individuals, in the last case, to be isolated from the equilibrated solution by fractional precipitation.

[90] S. Goldschmidt and W. Schmidt, *Ber.*, 1922, **55**, [*B*], 3197; *A.*, 1922,i, 1149.
[91] S. Goldschmidt and C. Steigerwald, *Annalen*, 1924, **438**, 202; *A.*, i, 1062.

C. K. Ingold.

Part III.—Heterocyclic Division.

Last year will probably prove a memorable year in the chemistry of alkaloids. It has witnessed the completion in detail of the synthesis of *l*-cocaine, the almost sensational proof that the "synthetic berberine" of Pictet and Gams is not berberine, but a structural isomeride, the synthesis of a complex base which may prove to be closely allied to strychnine, the completion of the interesting investigation of the Anhalonium alkaloids and the beginning of what looks like a general attack on the Chelidonium alkaloids. This Report has therefore been written with the work on alkaloids as its centre-piece with other work dovetailed into it where possible. For this reason, many important results, *e.g.*, those on heterocyclic compounds containing carbon–sulphur and carbon–oxygen, are not mentioned, but it is hoped to deal with these in future Reports.

Pyrrole Derivatives.

Mention was made in the previous Report of the large amount of work in progress on the synthesis of complex derivatives of pyrrole related to naturally-occurring substances or their degradation products, and the output of results in this direction shows no diminution this year.

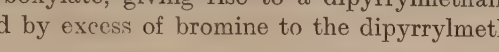
The ease with which β-phenylethyltrimethylammonium hydroxide decomposes quantitatively into styrene and the tertiary base has led to the investigation of this reaction as a means of preparing more complex tertiary bases, and in this way ethyl 1-β-phenylethylpyrrolidine-2 : 5-dicarboxylate, by conversion into the quaternary ammonium hydroxide, has been used for the production of 1-methylpyrrolidine in good yield.[1]

Di- and tri-substituted pyrroles with a free α-position, when treated with excess of bromine, yield crystalline dyes, which are mostly dipyrrylmethenes, produced by the loss of hydrogen bromide between the original substance and the dibromopyrrole first formed;[2] thus, the dye furnished by the action of bromine on ethyl 2 : 4-dimethylpyrrole-3-carboxylate results from the interaction of the hydrogen atom in position 5 in a molecule of the original substance and the bromine atom of the bromomethyl group in the first formed ethyl 5-bromo-4-methyl-2-bromomethyl-

[1] J. v. Braun and R. S. Cahn, *Annalen*, 1924, **436**, 262; *A.*, i, 632; compare *A.*, 1911, i, 611.

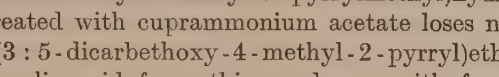
[2] Hans Fischer and H. Scheyer, *ibid.*, 1923, **434**, 237; *A.*, 1924, i, 80; compare *Ann. Reports*, 1923, **20**, 137.

pyrrole-3-carboxylate, giving rise to a dipyrrylmethane, which is then oxidised by excess of bromine to the dipyrrylmethene (I),



(I.)

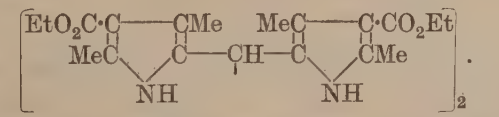
These initial halogenated pyrroles condense with aniline and with hydrazines, giving rise to complex derivatives. Thus ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate yields, with hydrazine, αα-di(3 : 5-dicarbethoxy-4-methyl-2-pyrrylmethyl)hydrazine, and this when treated with cuprammonium acetate loses nitrogen and forms *s*-di-(3 : 5-dicarbethoxy-4-methyl-2-pyrryl)ethane. The 5 : 5′-dicarboxylic acid from this condenses with formic acid in presence of hydrochloric acid to give 5 : 5′-di-(3″-carbethoxy-4″-methyl-2″-pyrrylmethyl)-4 : 4′-dicarbethoxy-3 : 3′-dimethyl-2 : 2′-dipyrrylmethene [3] (II). This tetrapyrrole derivative is



(II.)

intensely yellow in colour and closely resembles mesobilirubin,[4] $C_{32}H_{38}O_6N_4$, obtained by H. Fischer from bilirubin, one of the bile pigments.

The same author has embarked on the study of tetrapyrrylethanes with an investigation of the compound produced by the condensation of glyoxal with ethyl 2 : 4-dimethylpyrrole-3-carboxylate in alkaline- or acid-alcoholic solution and to which the following formula is assigned :



It gives an intensely green-coloured solution with acetic acid, is oxidised by ferric chloride to bis-3-carbethoxy-2 : 4-dimethylpyrrylmethene, and on reduction by hydriodic acid in acetic acid yields a mixture containing 2 : 4-dimethyl- and 2 : 4 : 5-trimethylpyrroles. The acid obtained by hydrolysis of the ester is different from that produced by direct condensation of glyoxal with 2 : 4-dimethylpyrrole-3-carboxylic acid.

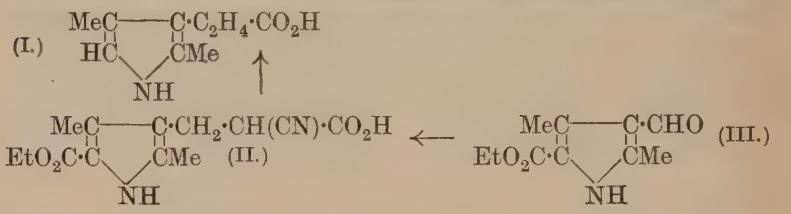
The evidence so far obtained indicates that the tetrapyrrylethanes

[3] Hans Fischer and H. Scheyer, *Annalen*, 1924, **439**, 185; *A.*, i, 1232.

[4] Hans Fischer, *Ber.*, 1914, **47**, 2330; *Z. Biol.*, 1914, **65**, 163; *A.*, 1914, i, 1135; 1915, i, 148.

are more closely related to the pigments of bile than to those of blood.[5]

The application of the Gattermann reaction to the preparation of aldehydes in the pyrrole series has been utilised by Fischer and his collaborators,[6] and among the interesting fission products of the blood pigment, hæmin, so prepared are cryptopyrrole- (I)[7] and phyllopyrrole-carboxylic acids.[8] The starting-point for the former was ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate (III), which was condensed with cyanoacetic acid, and the product reduced (II), hydrolysed, and decarboxylated successively at positions 3 and 5. 2 : 4 : 5-Trimethyl-3-(ω-cyano-ω-carboxyvinyl)-



pyrrole (corresponding to II before reduction) cannot be hydrolysed directly, but on melting loses carbon dioxide, forming 2 : 4 : 5-trimethyl-3(ω-cyanovinyl)pyrrole, which on reduction and hydrolysis yields phyllopyrrolecarboxylic acid (2 : 4 : 5-trimethylpyrrole-3(β)-propionic acid); the latter can also be obtained by the reduction of the 2 : 4 : 5-trimethylpyrrole-3(β)-acrylic acid formed when the pyrrole-3-aldehyde is condensed with malonic acid. The fission products of hæmin—cryptopyrrole, hæmopyrrole, and phonopyrrole—have also been used for the preparation of aldehydes and the latter for similar syntheses.[9]

Galegine, a supposed simple derivative of pyrollidine, which G. Tanret [10] isolated from *Galega officinalis*, has now been shown to be a derivative of guanidine to which G. Barger and F. D. White [11] assign the formula $CMe_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}C(:NH){\cdot}NH_2$ or possibly $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C(:NH){\cdot}NH_2$, whilst E. Späth and S. Prokopp [12] prefer the form $CMe_2{:}CH{\cdot}CH_2{\cdot}N{:}C(NH_2)_2$.

[5] Hans Fischer and M. Schubert, *Ber.*, 1923, **56**, [*B*], 2379; *A.*, 1924, i, 217; compare *Ann. Reports*, 1923, **20**, 138.

[6] Hans Fischer and J. Müller, *Z. physiol. Chem.*, 1924, **132**, 73; *A.*, i, 319; compare *Ann. Reports*, 1923, **20**, 137, and Angeli, *Ber.*, 1924, **57**, [*B*], 834; *A.*, i, 760.

[7] H. Fischer and B. Weiss, *Ber.*, 1924, **57**, [*B*], 602; *A.*, i, 543.

[8] H. Fischer and C. Nenitzescu, *Annalen*, 1924, **439**, 172; *A.*, i, 1233.

[9] Hans Fischer and M. Schubert, *Ber.*, 1924, **57**, [*B*], 610; *A.*, i, 544.

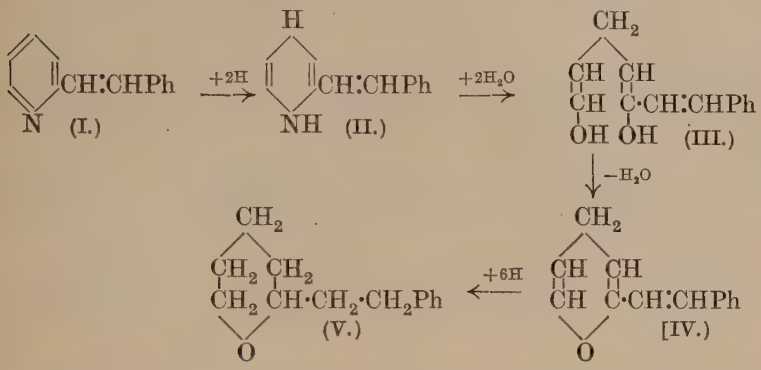
[10] *Compt. rend.*, 1914, **158**, 1182, 1426; *A.*, 1914, i, 721, 859; *Thesis*, Paris, 1917; *Bull. Soc. chim.*, 1924, [iv], **35**, 404; *A.*, i, 622.

[11] *Biochem. J.*, 1923, **17**, 827; *A.*, 1924, i, 272.

[12] *Ber.*, 1924, **57**, [*B*], 474; *A.*, i, 502.

Pyridine Derivatives.

B. D. Shaw [13] has shown that 2-stilbazole (I) in aqueous alcohol is reduced by sodium to 2-β-phenylethyltetrahydropyran (V) and the action is assumed to take place in the following way :



Pyridine itself is similarly converted into ammonia and traces of a volatile oil, which may be pentamethyleneoxide. Fission of the ring in this case also appears to take place after stage II, and it is suggested that the large amount of resin produced is due to the action of the alkali on glutardialdehyde (corresponding to stage III), formed when the ring is opened. P. Baumgarten [14] has found that the additive compound formed between pyridine and ethyl chlorosulphonate is transformed by aqueous sodium hydroxide into sodium sulphamate and the sodium salt of the enolic form of glutacondialdehyde, ONa·CH:CH·CH:CH·CHO; a second form of the sodium salt indicates that the aldehyde may also exist in the cyclic form, $CH\langle^{CH—O}_{CH:CH}\rangle CH\cdot OH$. The sodium salt is reconvertible into pyridine by boiling with ammonium acetate. The formation of pyridine bases by the passage of acetylene and ammonia over alumina heated at 400° has now been investigated in detail.[15] The products formed include pyrroles, α- and γ-picolines, β-collidine, and two other collidines, which are not identical with 4-methyl-2-ethyl pyridine, or 2 : 3 : 4- or 2 : 3 : 6-trimethylpyridine. A similar ring condensation occurs when acetylene is replaced by acetaldehyde, paraldehyde, or propionaldehyde.[16] These reactions,

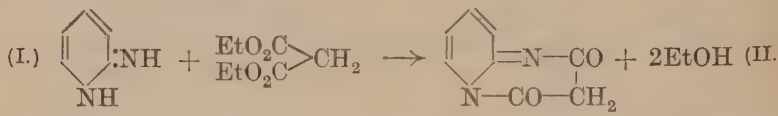
[13] *J.*, 1924, **125**, 1930; compare *Ann. Reports*, 1923, **20**, 147.

[14] *Ber.*, 1924, **57**, [*B*], 1622; *A.*, i, 1166.

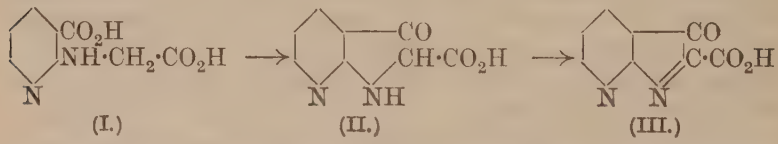
[15] A. E. Tschitschibabin and others, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 703; 1924, **54**, 607, 611; *A.*, 1915, i, 638; 1924, i, 313.

[16] *Idem, ibid.*, 1924, **54**, 601; *A.*, i, 312; *J. pr. Chem.*, 1924, [ii], **107**, 132, 138, 145, 154; *A.*, i, 766, 767; O. Seide, *Ber.*, 1924, **57**, [*B*], 791; *A.*, i, 767.

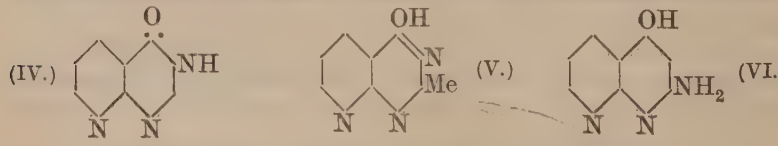
supplemented by the sodamide method [17] for introducing the amino-group into the resulting and other bases, have provided means for the synthesis of a series of substituted pyridines and quinolines. Since 2-phenoxypyridine is convertible into 1-phenyl-pyridone at a red heat, it seems clear that direct conversion of tautomeric forms is possible and is not limited to indirect formation through quaternary halides.[18] The sodium salt of 2-pyridone is transformed by carbon dioxide under pressure at 180—200° into 2-hydroxypyridine-5-carboxylic acid.[19] 2-Aminopyridine appears to be capable of acting in the sense of the tautomeric pyridone-2-imine (I) form, since it condenses with ethyl malonate to form 4 : 6-diketo-1 : 2-divinylene-1 : 4 : 5 : 6-tetrahydropyrimidine [20] (malonyl-α-aminopyridine) (II). According to E. Sucharda [21]



2-aminonicotinic acid condenses with chloroacetic acid in presence of potassium carbonate to give a good yield of pyridylglycine-carboxylic acid (I), which is converted by mineral acids into 3-keto-2 : 3-dihydro-1 : 7-benzdiazole-2-carboxylic acid (II); and this on oxidation by permanganate yields the dehydro-compound (III): this constitutes the first synthesis of a pyridopyrrole, analogous to indole.



2-Aminonicotinic acid also condenses with formamide and acetamide, giving small yields of 4-hydroxy-1 : 3 : 8-benztriazine (IV) and its 2-methyl derivative, respectively. The second of these is readily soluble in water, acids, or alkalis, and is consequently believed to have the lactim structure (V). The alternative structure



[17] A. E. Tschitschibabin, *D.R.-P.* 374291, with Kirssanov, *Ber.*, 1924, **57**, [*B*], 1163; *A.*, i, 203, 978; compare *Ann. Reports*, 1923, **20**, 146.

[18] A. E. Tschitschibabin and N. P. Jeletzky, *Ber.*, 1924, **57**, [*B*], 1158; *A.*, i, 987.

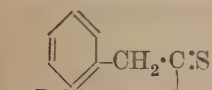
[19] A. E. Tschitschibabin and A. W. Kirssanov, *ibid.*, 1161; *A.*, i, 988.

[20] A. E. Tschitschibabin, *Ber.*, 1924, **57**, [*B*], 1168; *A.*, i, 987.

[21] *Roczniki Chemji*, 1923, **3**, 236; *A.*, 1924, i, 881.

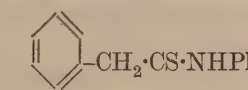
(VI) is untenable, as the parent substance shows none of the reactions of a primary amine and differs from the methyl derivative mainly in showing more acidic characters.[22]

Mention was made in the previous Report [23] of the isolation of pyridine methides resulting from the action of sodium hydroxide on pyridine methosulphate. Similar products had already been made by W. Schneider and his collaborators,[24] who have now described a number of their characteristic reactions. They were prepared by treating quaternary salts of α- or γ- methylated pyridines (or quinolines) with alkali; thus α-picoline methosulphate yields *N*-methyl-α-methylenedihydropyridine, and γ-picoline the corresponding γ-methylenedihydropyridine. These substances combine with carbon disulphide, phenylthiocarbimide or phenylcarbimide to form compounds of the following types (α-picoline derivatives), (I) representing the compound formed with carbon disulphide



(I.)

(II.)



(III.)

and (II) that with phenylthiocarbimide, whilst (III) represents the salts (addition of HX) formed by compounds of type (II) with acids. These additive products are well-crystallised substances, and the formulæ are in harmony with the facts that they are stable to acids, but not to cold permanganate solution,[25] although E. Rosenhauer [26] formulates what appear to be strictly analogous carbon disulphide additive products, derived from quinoline, somewhat differently.

Similarly 1 : 4 : 6-triphenyl-2-methylpyridinium iodide, obtained by treating 4 : 6-diphenyl-2-methylpyrylium iodide with aniline, when treated with alkali furnishes the corresponding anhydro-base, 1 : 4 : 6-triphenyl-2-methylenedihydropyridine. The latter forms additive compounds with the three reagents mentioned above, and this is also true of a series of similar substances prepared at the same time.[27] The first of these products made was obtained by

[22] L. Klisiecki and E. Sucharda, *Roczniki Chemji*, 1923, **3**, 251; *A.*, 1924, i, 883.

[23] *Ann. Reports*, 1923, **20**, 147.

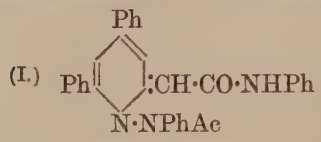
[24] W. Schneider and F. Seebach, *Ber.*, 1921, **54**, [*B*], 2285; *A.*, 1921, i, 877; H. Decker, *ibid.*, 1905, **38**, 2493; *A.*, 1905, i, 667.

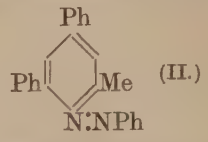
[25] W. Schneider, K. Gaertner, and A. Jordan, *ibid.*, 1924, **57**, [*B*], 522; *A.*, i, 551.

[26] E. Rosenhauer and others, *ibid.*, p. 1291; *A.*, i, 1236 (analogous quinoline compounds); *J. pr. Chem.*, 1924, [ii], **107**, 232; *A.*, i, 768.

[27] W. Schneider and others, *Annalen*, 1924, **438**, 115, 147; *A.*, i, 1107, 1109.

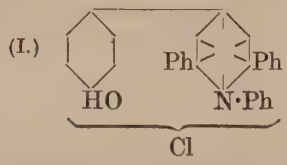
the action of phenylhydrazine on 4 : 6-diphenyl-2-methylpyrylium iodide, and the anhydro-base obtained from it by the action of alkali was formulated as 1-phenylamino-4 : 6-diphenyl-2-methylene-dihydropyridine (I, as the phenylcarbimide additive product [28] of the acetyl derivative). It behaves in some reactions as such, but

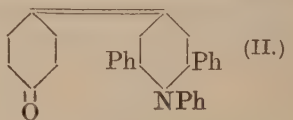




is unusual in being intensely blue in colour instead of red or yellow, and although it combines with carbon disulphide, etc., it does so slowly, and it adds on 2 mols. of phenylcarbimide. It is believed that in this case the presence of a phenyl group in position 4 so modifies the valency distribution as to convert the substance into a pyridinephenylimine (II), although it may act as a methylene base due to tautomeric change.

When 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride is treated with aniline, it yields 1 : 2 : 6-triphenyl-4-*p*-hydroxyphenyl-pyridinium chloride ($C_{29}H_{22}ONCl,0{\cdot}5HCl$, bright yellow), which, on heating, gives the neutral chloride ($C_{29}H_{22}ONCl$, dark red), and this with boiling alcoholic ammonia furnishes a dihydrate of the dark red anhydro-base, 1 : 2 : 6-triphenyl-4-quino-1 : 4-dihydro-pyridine. The yellow chloride is believed to have the benzenoid structure (I) and the anhydro-base the quinonoid constitution [29] (II).





Comparatively little work has been done on naturally-occurring pyridine compounds, but the interesting new observation has been made that trigonelline,[30] so far only found in plants, occurs in one of the sea-urchins (*Arbatia pustulosa*), the only simple pyridine compound so far recorded in marine animals being pyridine metho-hydroxide.

[28] W. Schneider and others, *Ber.*, 1921, **54**, [*B*], 2285; 1922, **55**, [*B*], 2775; *A.*, 1921, i, 877; 1922, i, 1171.

[29] W. Dilthey and others, *J. pr. Chem.*, 1924, [ii], **107**, 7; *A.*, i, 553; compare *A.*, 1920, i, 448; 1921, i, 735; 1922, i, 272.

[30] F. Holtz and others, *Z. Biol.*, 1924, **81**, 57; *A.*, i, 907; compare also D. Ackermann and others, *ibid.*, 1924, **81**, 61; *A.*, i, 243, 978; compare *A.*, 1923, i, 1155.

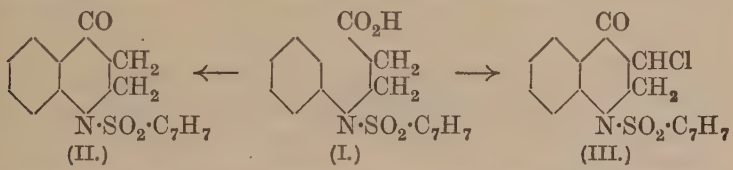
Quinoline Group.

Much of the work published on quinoline derivatives is mainly of technical interest.

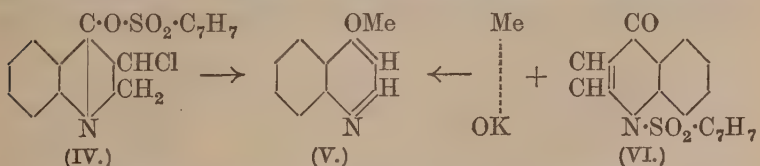
When *ar*-β-tetrahydronaphthylamine is used for the quinaldine synthesis, both the linear (6 : 7-tetramethylenequinaldine) and the angular (5 : 6-tetramethylenequinaldine) compounds are formed; the yield of both is increased by high concentration of hydrochloric acid.[31]

Further evidence of the intermediate formation of anils in Skraup's quinoline synthesis [32] is afforded by the observation that methyl*iso*propenylaniline, obtained from acetoneanil and methyl sulphate, is converted by cyanoacetic or chloroacetic acid into the dimeride, which is transformed by dry hydrogen chloride at 180—200° into 2 : 4-dimethylquinoline.[33]

4-Tetrahydroquinolone [34] has been synthesised by condensing toluene-*p*-sulphonanilide with β-chloropropionic acid to toluene-*p*-sulphonyl-β-anilinopropionic acid (I), which is then dehydrated with phosphoric oxide in boiling xylene to toluene-*p*-sulphonyl-4-tetrahydroquinolone (II), and this on hydrolysis gives 4-tetrahydroquinolone. If, however, substance (I) is digested with phosphoryl chloride, dehydration (with ring closure) and chlorination occur and toluene-*p*-sulphonyl-3-chloro-4-tetrahydroquinolone (III) is formed. The latter on prolonged ebullition with hydrochloric acid loses the toluene-*p*-sulphonyl group, and the chlorine atom is simultaneously replaced by hydrogen, also giving 4-tetrahydroquinolone.



On digestion with methyl-alcoholic potassium hydroxide, substance (III) is quantitatively converted into 4-methoxyquinoline (V). Two suggestions are offered in explanation of this reaction, (*a*) that



[31] J. Lindner and others, *Monatsh.*, 1924, **44**, 337; *A.*, i, 1102; compare v. Braun and Grubet, *Ber.*, 1922, **55**, [*B*], 1710; *A.*, 1922, i, 762.

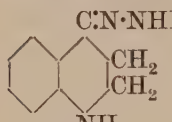
[32] Compare *Ann. Reports*, 1923, **20**, 149.

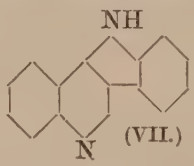
[33] E. Knoevenagel and others, *Ber.*, 1923, **56**, [*B*], 2414; *A.*, 1924, i, 205.

[34] G. R. Clemo and W. H. Perkin, jun., *J.*, 1924, **125**, 1608.

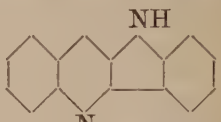
the toluene-*p*-sulphonyl group migrates to position 4, forming an ester (IV), which then reacts to give the methyl ether (V) or (*b*) that an unstable dihydro-derivative (VI) is formed by removal of hydrogen chloride, which passes into the stable 4-methoxyquinoline. This method of synthesis is not general and 2-methyltetrahydroquinolone could not be obtained by replacing β-chloropropionic acid by β-chlorobutyric acid.

4-Tetrahydroquinolone is a highly reactive substance. The phenylhydrazone undergoes the Fischer indole reaction, but oxidation also takes place producing 3 : 4-quinindoline (VII) isomeric with ordinary 2 : 3-quinindoline (VIII). It also condenses with isatin to form dihydro-2 : 3-quinoquinoline-4-carboxylic acid (IX), which has not been isolated, as it loses carbon dioxide at 210°,



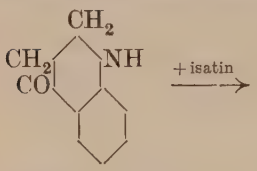


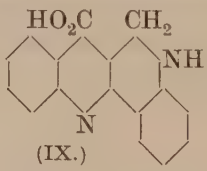
(VII.)



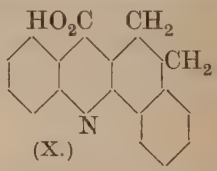
(VIII.)

giving the dihydro-base, and this on distillation over lead oxide gives 2 : 3-quinoquinoline. The special interest of this condensation





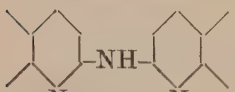
(IX.)



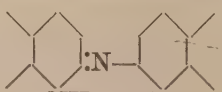
(X.)

product is that it resembles in structure J. von Braun and P. Wolff's 5 : 6-dihydro-α-naphthacridine-7-carboxylic acid[35] (X), which exhibits some of the pharmacological properties of strychnine (compare p. 143).

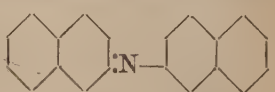
When 2-aminoquinoline is heated with 2-chloroquinoline, the hydrochloride of 2 : 2′-diquinolylamine, which exists in two modifications (I) and (II), is formed,[36] as would be expected on the grounds advanced by Scheibe to explain dimorphism in the cyanine



(I.)



(II.)



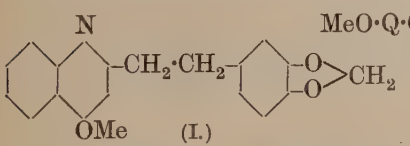
(III.)

[35] *Ber.*, 1922, **55**, [*B*], 3675; *A.*, 1923, i, 143; compare J. von Braun and A. Stuckenschmidt, *ibid.*, 1923, **56**, [*B*], 1724; *A.*, 1923, i, 947.

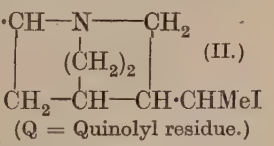
[36] Miss F. M. Hamer, *J.*, 1924, **125**, 1348; compare E. Diepolder and others, *J. pr. Chem.*, 1923, **106**, 41; *A.*, 1924, i, 994.

series.[37] Methyl iodide converts this substance into a mixture of 2 : 2′-diquinolylamine hydriodide (I) and 1-methyldihydroquinolenyl-2-quinolyl-2′-imine methiodide (III) (now named 1 : 1′-dimethylazocyanine iodide, the two quinoline residues being linked by :N· instead of by :CH· as in *iso*cyanine). The latter forms a mixture of orange and yellow crystals, both having the same melting point and absorption spectra and therefore probably being geometrical isomerides. Comparison with the analogous 1 : 1′-dimethyl-ψ-*iso*cyanine iodide (red) shows that the replacement of :CH· by :N· causes a shift of the absorption bands towards the more refrangible end of the spectrum.

Angostura Alkaloids.—From angostura or cusparia bark three well-characterised alkaloids, *viz.*, cusparine, $C_{19}H_{17}O_3N$, galipine, $C_{20}H_{21}O_3N$, and galipoidine, $C_{19}H_{15}O_4N$, have been isolated. For galipine, Tröger and Kroseberg[38] suggested a formula which represents it as 7-methoxy-4(β)-3′ : 4′-dimethoxyphenylethylquinoline. E. Späth and O. Brunner[39] have now synthesised the latter substance by condensing *m*-methoxyaniline with ethyl acetoacetate to 2-hydroxy-7-methoxy-4-methylquinoline and converting this through the 2-chloro- derivative into 7-methoxy-4-methylquinoline, which with 3 : 4-dimethoxybenzaldehyde in presence of zinc chloride yielded 7-methoxy-4(β)-3′ : 4′-dimethoxyphenyl-Δ^{α}-ethinylquinoline; this on reduction with hydrogen in presence of palladinised charcoal gave the product sought. Neither it nor the isomeric 2(β)-3′ : 4′-dimethoxyphenylethylquinoline compound proved identical with galipine and the clue to the constitution of the alkaloid was found in Tröger's observation that galipine on oxidation yields an acid, $C_{11}H_9O_3N$, which is probably a methyl ether of the similar acid, $C_{10}H_7O_3N$, produced by the oxidation of cusparine. It was surmised that this acid was 4-methoxyquinoline-2-carboxylic acid and with this in mind 4-methoxy-2-methylquinoline was condensed with piperonal and the resulting base reduced, when cusparine resulted. Cusparine must therefore be 4-methoxy-2(β)-3′ : 4′-methylenedioxyphenylethylquinoline (I), and the obvious conclusion that galipine must be cusparine with the methylenedioxy-



(I.)



(II.)

(Q = Quinolyl residue.)

[37] G. Scheibe and others, *Ber.*, 1920, **53**, [*B*], 2064; 1921, **54**, 786; *A.*, 1921, i, 62, 451.

[38] *Arch. Pharm.*, 1912, **250**, 494; *A.*, 1912, i, 895.

[39] *Ber.*, 1924, **57**, [*B*], 1243; *A.*, i, 1226.

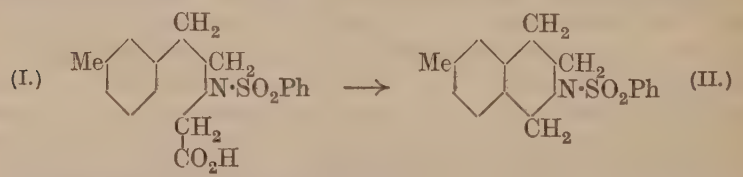
group replaced by two methoxy-groups has been confirmed by the synthesis of galipine from 4-methoxy-2-methylquinoline and 3 : 4-dimethoxybenzaldehyde.[40]

Matrine, $C_{15}H_{24}ON_2$, was isolated from *Sophora angustifolia* by Plugge in 1895, and has recently been worked at by H. Kondo [41] and his colleagues, whose results so far are mainly of interest in indicating some similarity in structure between matrine and cytisine, the typical alkaloid of the genus.

Quinine.—K. W. Rosenmund and E. Kittler [42] have shown that hydriodoquinine, $C_{20}H_{25}O_2N_2I$, is a mixture of two isomeric bases (*a*), having $[\alpha]_D - 74{\cdot}3°$, and (*b*), having $[\alpha]_D - 128{\cdot}3°$. The former on reduction gives dihydroquinine and is represented by formula II, whilst in (*b*), which reduces to niquine (nichin), $C_{20}H_{24}O_2N_2$, the quinuclidine bridge is probably ruptured as suggested by Léger [43] for niquine.

iso*Quinoline Derivatives*.

A new method [44] for the preparation of tetrahydro*iso*quinoline and its ring homologues consists in treating acyl derivatives of substituted glycine with phosphorus pentachloride and aluminium chloride successively, *e.g.*, β-*m*-tolylethylbenzenesulphonylglycine (I) can in this way be converted into 2-benzenesulphonyl-6-methyltetrahydro*iso*quinoline (II). The yields are stated to be good.



6-Methoxytetrahydro*iso*quinoline has also been synthesised by a routine method.[45]

Of the seven alkaloids present in Anhalonium species the constitutions of five are known,[46] since either they or their methyl ethers have been synthesised. The two remaining bases, anhalonine and lophophorine, have now been prepared by E. Späth and J. Gangl.[47] The former is 6-methoxy-7 : 8-methylenedioxy-1-

[40] E. Späth and H. Eberstaller, *Ber.*, 1924, **57**, [*B*], 1687; *A.*, i, 1335.

[41] K. Kondo and others, *J. Pharm. Soc. Japan*, 1899, No. 84; 1903, Nos. 260—262; 1921, pp. 659, 1047; 1923, No. 498, p. 644; *A.*, 1921, i, 882; 1922, i, 269; 1924, i, 76.

[42] *Arch. Pharm.*, 1924, **262**, 18; *A.*, i, 982.

[43] *Compt. rend.*, 1919, **169**, 797; *A.*, 1919, i, 597.

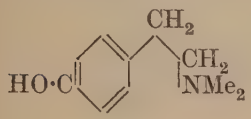
[44] J. von Braun and others, *Ber.*, 1924, **57**, [*B*], 908; *A.*, i, 873.

[45] L. Helfer, *Helv. Chim. Acta*, 1924, **7**, 945; *A.*, i, 1341.

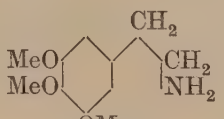
[46] *Ann. Reports*, 1922, **19**, 162; 1923, **20**, 154.

[47] *Monatsh.*, 1923, **44**, 103; *A.*, 1924, i, 69.

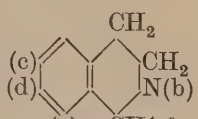
methyltetrahydro*iso*quinoline and the latter is the *N*-methyl derivative of this. The seven alkaloids form an interesting series : (I) hordenine, (II) mezcaline, (III) anhalamine, (IV) anhalonidine *O*-methyl ether, (V) pellotine *O*-methyl ether, (VI) anhalonine, (VII) lophophorine.



(I.)



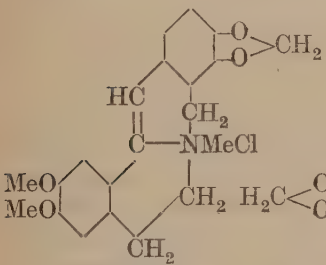
(II.)



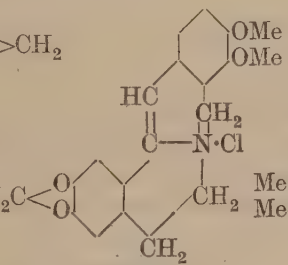
(III.) to (VII.)

In III, a = H, b = H, c, d, and e, = HO, OMe, OMe
In IV, a = Me, b = H, c, d, and e = OMe.
In V, a = Me, b = Me, c, d, and e = OMe.
In VI, a = Me, b = H, c = OMe, d and e = ·O·CH_2·O.
In VII, a = Me, b = Me, c = OMe, d and e = ·O·CH_2·O.

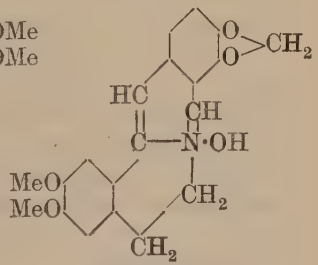
Berberine and Allied Alkaloids.—In assigning a formula to cryptopine, one of the many data used was the fact that it was possible to convert the alkaloid through *iso*cryptopine into *epi*-berberine, a substance which only differs from berberine by the interchange of positions between the piperonyl and veratryl residues as shown by the following formulæ.[48]



iso*Cryptopine chloride.*



Berberinium chloride.

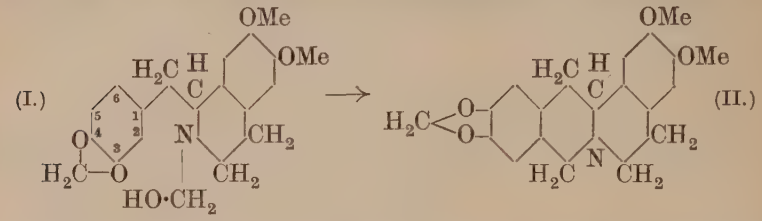


epi*Berberinium hydroxide.*

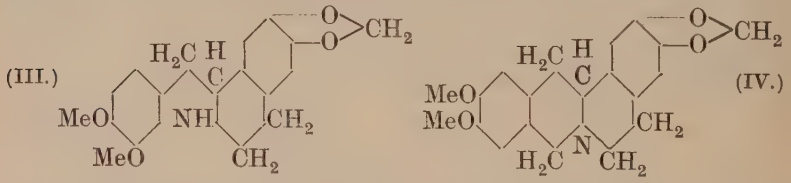
It ought therefore to be possible to apply the method of Pictet and Gams [49] for the synthesis of berberine to the preparation of *epi*berberine, but it was found [50] that, using the formyl derivative of 1-homopiperonyl-6 : 7-dimethoxytetrahydro*iso*quinoline (I) in this way, the substance obtained was not the expected *epi*berberine but an isomeride, which is named tetrahydroanhydro-ψ-*epi*berberine

[48] W. H. Perkin, jun., *J.*, 1918, **113**, 492.
[49] *Compt. rend.*, 1911, **153**, 386; *A.*, 1911, *i*, 807.
[50] J. S. Buck and W. H. Perkin, jun., *J.*, 1924, **125**, 1675.

(II), condensation having taken place, with the aid of the nitrogen group, at position 6 in place of position 2 as in the supposed ber-



berine synthesis. This new base yields a series of derivatives analogous to, and isomeric with, but different from those furnished by tetrahydroanhydro*epi*berberine. It then became of interest to ascertain, if possible, why the reaction proceeded differently in the case of 1-veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline (III), the material used by Pictet and Gams in the synthesis of berberine, but on repeating this work it was found that the substance produced was not tetrahydroanhydroberberine, but an isomeride of this, *viz.*, tetrahydroanhydro-ψ-berberine (IV), condensation having taken place in this instance also at position 6 instead of position 2.

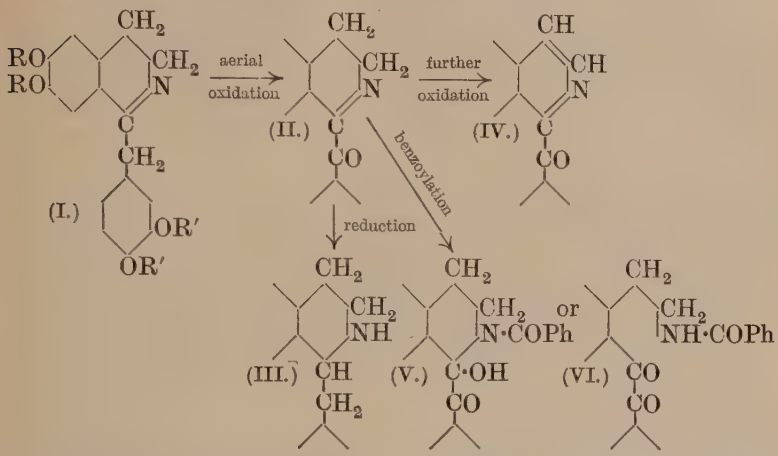


This again gives a series of derivatives analogous to, and isomeric with, but different from those of berberine. Similarly, repetition of Pictet and Gams's experiments in the synthesis of oxyberberine failed to yield the latter base or indeed any crystallisable product.[51]

In the course of the work just described, it was noticed [52] that the 6 : 7-dimethoxy-3′ : 4′-methylenedioxy-1-benzoyl-3 : 4-dihydro-*iso*quinolines (I) and the corresponding 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-compounds, all of empirical formula $C_{19}H_{17}O_4N$, readily oxidised on exposure in solution to the atmosphere, forming bases of the formula $C_{19}H_{17}O_5N$ (II). The latter are (*a*) reducible by tin and hydrochloric acid to the corresponding substituted benzyltetrahydro*iso*quinolines (III), and (*b*) oxidised by boiling with methyl-alcoholic potassium hydroxide, losing two atoms of hydrogen from positions 3 and 4, giving bases of type IV. On benzoylation, in presence of alkali, compounds of type II (initial oxidation

[51] R. D. Haworth, W. H. Perkin, jun., and J. Rankin, *J.*, 1924, **125**, 1686.
[52] J. S. Buck, R. D. Haworth, and W. H. Perkin, jun., *ibid.*, p. 2176.

products) take up the elements of one molecule of benzoic acid, and the new derivatives (formulated as type V or VI; the latter being considered the more probable), on digestion with acid, lose benzoic acid and form salts of the original bases (type II).

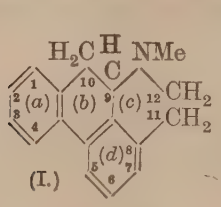


Papaveraldine, the first oxidation product of the alkaloid papaverine, is a base of type IV, and in conformity with that view it was found that 6 : 7 : 3′ : 4′-tetramethoxy-1-benzyl-3 : 4-dihydro-*iso*quinoline (formula I, where R and R′ = Me) oxidised on exposure to air to a base $C_{20}H_{21}O_5N$ (Type II), and this on digestion with methyl-alcoholic potassium hydroxide gave papaveraldine (Type IV).

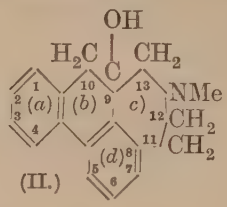
Chelidonium Alkaloids.—Seven alkaloids occur in the greater celandine (*Chelidonium majus*), of which one, methoxychelidonine, is new, and six, old and well-known, *viz.* (*a*) protopine and *allo*cryptopine (β- and γ-homochelidonines), for which formulæ have been proposed, and (*b*) chelidonine, homochelidonine, chelerythrine, and sanguinarine. Formulæ are now proposed for the first two of group *b*. Further, it is known that homochelidonine can be converted into chelerythrine, and it has now been established that "sanguinarine" is a mixture of chelerythrine and a dehydrochelidonine or ψ-chelerythrine, obtained by the gentle oxidation of chelidonine. This second group of four alkaloids is the subject of a series of long papers by J. Gadamer and his pupils.[53] They belong to what has been called the phenanthrene group of *iso*quinoline alkaloids, of which *apo*morphine is perhaps the best known example. What may be regarded as the parent of this

[53] *Arch. Pharm.*, 1919, **257**, 298; 1920, **258**, 148; 1924, **262**, 249; *A.*, 1920, i, 75, 872; 1921, i, 579; 1924, i, 1227; also *ibid.*, 1924, **262**, 452, 501, 578.

group has been synthesised and christened aporphine (I), but has not yet been described. It is proposed to re-name the

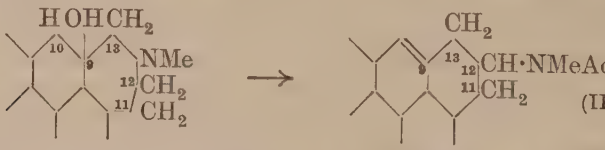


(I.)



(II.)

group after it. Formula II represents chelidonine, $C_{20}H_{19}O_5N$, with a dioxymethylene group in ring (*a*), possibly at positions 2 and 3, and another in ring (*d*), possibly at 5 and 6. The new alkaloid, methoxychelidonine, has, in addition, a methoxyl group, probably at 1, and homochelidonine differs from chelidonine only in having two methoxyl groups in place of one of the dioxymethylene groups. It will be seen that formula II is based on Pschorr's *apo*morphine formula with the new feature of a 7-ring (*c*). In its reactions chelidonine presents a general resemblance to other members of the group to which it is assigned. Thus on exhaustive methylation it produces trimethylamine and a substance, $C_{19}H_{14}O_4$, regarded as a phenanthrene derivative. By the action of hot acetic anhydride, 1 mol. of water is lost and *N*-acetylanhydrochelidonine, $C_{22}H_{19}O_5N$, is formed, indicating that a tertiary nitrogen atom originally present has been converted into a secondary, probably by the opening of ring (*c*) between the NMe and C (13) positions, and re-closing of the ring between C (13) and C (12). The loss of water takes place between C (10) and C (9); this last step also explains the disappearance of optical activity in this reaction, the final position being represented by partial formula III. A similar change takes place



(III.)

when chelidonine is methylated, two methines, A and B, being formed, which are regarded as stereoisomeric, C (12) becoming asymmetric, and their formation is regarded as again due to the opening and reclosing of ring (*c*) as described above, the side chain, $\cdot CH\cdot NMe_2$, being formed at position 12.

Among the considerations which led to the adoption of this formula for chelidonine and its allies, including protopine and *allo*cryptopine, is the suggestion that these types of alkaloid might be formed in plants by the interaction of phenylacetaldehyde,

N-methylphenylethylamine, and formaldehyde, and two schemes whereby this condensation might occur are discussed.

Derivatives of Tropane and Granatane.

Much of the work done in these two groups centres round the production of local anæsthetics. R. Willstätter, O. Wolfes, and H. Mäder [54] have found that methyl tropinonecarboxylate on reduction yields three out of the four possible racemic methylecgonines. One of these on benzoylation furnishes *r*-cocaine, from which *d*-cocaine and *l*-cocaine, the latter identical with the natural alkaloid, were obtained by fractional crystallisation of the hydrogen *d*-tartrates. A second *r*-methylecgonine was deracemised by the use of *d*-α-bromocamphor-β-sulphonic acid, and the resolved products on benzoylation furnished *l*- and *d*-ψ-cocaines, the latter being identical with Einhorn's *d*-cocaine made from *d*-ecgonine (now called *pseudo*ecgonine), produced by the action of alkali on ordinary *l*-ecgonine from natural *l*-cocaine. The third racemate has not been fully examined. According to R. Gottlieb, ψ-configuration in the cocaines favours local anæsthetic action, the most powerful of the forms referred to above being *d*-ψ-cocaine. In both series, the *d*-form acts less powerfully than the *l*-form on the central nervous system, and on this and other grounds it has been suggested that *d*-ψ-cocaine may not be habit-forming; but recent pharmacological and clinical trials in this country indicate that it may not prove to have much, if any, practical advantage over ordinary *l*-cocaine as a local anæsthetic.[55]

Little success has so far attended attempts to improve cocaine as an anæsthetic by the replacement of benzoyl by other acyl groups, but W. Steinkopf and W. Ohse state that thiophen-2-carboxylic acid produces a "thiophen isologue" as active as cocaine and less toxic.[56] The corresponding "thiophenatropine" has also been made.[57]

S. Fränkel and G. Gruber have observed that with excess of magnesium methyl iodide in ice-cold ethereal solution cocaine (I) yields phenyldimethylcarbinol and tropyldimethylcarbinol: the latter and certain of its salts are local anæsthetics.[58]

In this connexion may also be mentioned S. M. McElvain's [59] comparison of ethyl 4-benzoyloxy-1-methylpiperidine-3-carboxylate

[54] *Annalen*, 1923, **434**, 111; *A.*, 1924, i, 70; compare E. Merck, *Brit. Pat.* 210050; *A.*, i, 870.

[55] Watson-Williams, *Brit. Med. J.*, 1925, i, 11; Copeland, *ibid.*, p. 9.

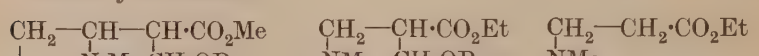
[56] *Annalen*, 1924, **437**, 14; *A.*, i, 661.

[57] W. Steinkopf and A. Wolfram, *ibid.*, p. 22; *A.*, i, 661.

[58] *Ibid.*, 1923, **433**, 241; *A.*, 1924, i, 72.

[59] *J. Amer. Chem. Soc.*, 1924, **46**, 1721; *A.*, i, 985.

(II) with the corresponding open-chain compound, β-carbethoxyethyl-γ-benzoyloxypropylmethylamine (III). The first is less active as an anæsthetic than cocaine and as toxic, and the second is scarcely anæsthetic.



(I.) (II.) (III.)

β-Eucaine, one of the best known partial substitutes for cocaine, and its isomeride, *iso*-β-eucaine, produced by the benzoylation of α- and β-vinyldiacetonalkamines (4-hydroxy-2 : 2 : 6-trimethylpiperidines), respectively, have been deracemised by H. King.[60] The details of both resolutions present a number of interesting features. The racemic forms and their optically active components are all equally active on the rabbit's cornea, but on the sciatic nerve of the frog β-eucaine is more powerful than *iso*-β-eucaine : the *l*-form of β-eucaine is more toxic than the *d*-form.

By an extension of the method used for the synthesis of tropinone,[61] R. C. Menzies and R. Robinson have prepared ψ-pelletierine (*N*-methylgranatonine) (I), a ring homologue of tropinone, from glutardialdehyde, methylamine, and calcium acetonedicarboxylate. Adipdialdehyde yielded a base having the properties of a homo-ψ-pelletierine.[62] These syntheses afford a further confirmation of Robinson's views as to the mode of origin of alkaloids in plants.[61]

S. M. McElvain and R. Adams have produced an interesting variant on *N*-methylgranatonine by synthesising ethyl *iso*granatoninecarboxylate (II). On reduction, it yields the corresponding alcohol, ethyl granatolinecarboxylate, and this on benzoylation furnishes an isomeride of a homococaine; it is more toxic and less potent as an anæsthetic than cocaine.[63]

(I.) (II.)

Derivatives of Indole and Carboline.

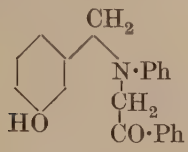
Although tertiary amino-ketones of the type

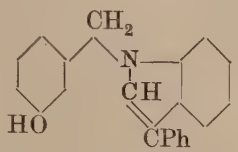
$$CH_2Ph{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}R,$$

where R may be an aryl or alkyl radical, should undergo intramolecular condensation producing either indoles or *iso*quinolines, the former are exclusively formed even when substituents favourable

[60] *J.*, 1924, **125**, 41. [61] Compare *Ann. Reports*, 1917, **14**, 134.
[62] *J.*, 1924, **125**, 2163.
[63] *J. Amer. Chem. Soc.*, 1923, **45**, 2738; *A.*, 1924, i, 417.

to *iso*quinoline formation are present; thus *m*-hydroxybenzylaniline, when condensed with ω-bromoacetophenone by phosphorus pentoxide in hot xylene, furnishes 1-*m*-hydroxybenzyl-3-phenylindole (I), and this on distillation with zinc dust is converted into *m*-cresol and 2-phenylindole.[64]



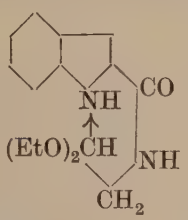


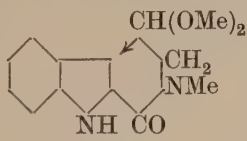
(I.)

Catalytic hydrogenation of indole takes place in much the same way as with quinoline,[65] addition of hydrogen to the heterocyclic nucleus occurring first, although substituents in either ring increase its resistance. In some cases, action proceeds further; thus, 2 : 5-dimethylindole yields as chief product *o*-propyl-*p*-toluidine, and 2 : 4 : 7-trimethylindole gives 3 : 6-dimethyl-2-propylaniline, and in most cases complete decomposition with evolution of ammonia occurs to some extent.

The alkaloids harmine and harmaline are derivatives of 6-methoxyindole, and the probability that indoles occur in other complex natural products lends special interest to the synthesis of a series of these compounds and their derivatives.[66] It had been shown previously [67] that whilst indole-2-carboxyacetalylamide (I), when warmed with hydrochloric acid, forms 5-keto-4 : 5-dihydroindolediazine(1 : 4), indole-2-carboxydimethylacetalylmethylamide (II) yields 3-keto-4-methyl-3 : 4-dihydro-4-carboline, condensation taking place in the direction indicated by the arrows. On extending

(I.)





(II.)

this reaction to 6-methoxyindoles, it was found that the methoxy-group appeared to favour azine condensation (I), since 6-methoxy-

[64] K. H. Bauer and K. Bühler, *Arch. Pharm.*, 1924, **262**, 128; *A.*, i, 985.

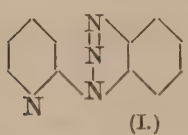
[65] J. von Braun and others, *Ber.*, 1924, **57**, [*B*], 392; *A.*, i, 545; compare *Ann. Reports*, 1923, **20**, 149, 150.

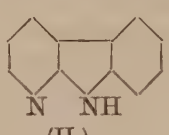
[66] K. G. Blaikie and W. H. Perkin, jun., *J.*, 1924, **125**, 296.

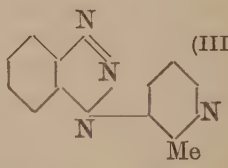
[67] W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *J.*, 1921, **119**, 1626; 1922, **121**, 1874. For numbering of carboline rings, see *J.*, 1919, **115**, 970; 1921, **119**, 1642; compare *Ann. Reports*, 1922, **19**, 128.

indole-2-carboxydimethylacetalylmethylamide yields both azine and carboline, but examination of other cases involving 4-, 5-, 6-, and 7-methoxyindoles has given results indicating that the methoxyl group is not the dominant factor, except perhaps when it occupies position 7, and that the chief factor influencing the direction of ring closure is the *N*-methyl group in the side chain, its presence facilitating carboline formation.

W. Lawson, W. H. Perkin, jun., and R. Robinson [68] have investigated a number of methods for the preparation of polynuclear systems allied to harmine. The similarity of carbazole to harmine suggested the trial of known methods of preparing carbazole to that of synthesising carbolines. Delétra and Ullmann's method [69] proceeds smoothly in simple cases, *e.g.*, 2-chloropyridine condenses readily with *o*-phenylenediamine to give *N*-α-pyridyl-*o*-phenylenediamine, which with nitrous acid yields 1-α-pyridylbenzotriazole (I). The latter, though more stable than the corresponding benzenoid bases, yields 3-carboline (II) when heated, in small quantities, with zinc chloride or phosphoric acid. Similarly, from


(I.)


(II.)

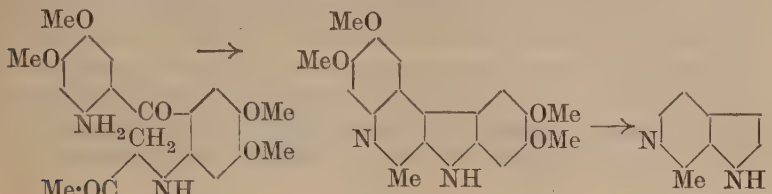

(III.)

2-chloroquinoline, benzo-3-carboline was prepared, and it was shown to be identical with Gabriel and Eschenbach's [70] "quindoline." R. Robinson and S. Thornley have applied the same method to the preparation of 5-carboline [71] from *N*-γ-pyridyl-*o*-phenylenediamine, obtained from 4-chloropyridine.

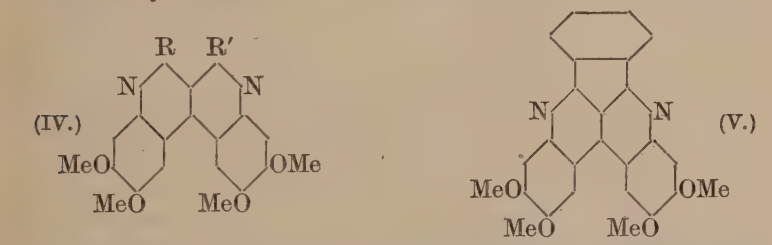
It may therefore prove to be a general method of obtaining carbolines, but, unfortunately, the triazole (III) which could probably be transformed into harmine could not be made owing to the non-reactivity of halogens in the β-position in the pyridine ring. Condensation of 3-aminoquinaldine and 3-amino-2-methylpyridine with appropriate chloronitrobenzenes was also tried, but without success. *apo*Harmine has, however, been synthesised by a novel process. 6 : 6′-Dinitro-3 : 4 : 3′ : 4′-tetramethoxybenzophenone was reduced and the resulting diaminoveratrone condensed in acetic acid with bromoacetone; the first product (I) of this action, treated with alkali, formed methyldiveratroharmyrine (II), and this after demethylation was oxidised by chromic acid to a

[68] *J.*, 1924, **125**, 626.
[69] *Arch. Sci. phys. nat.*, 1904, [v], **17**, 78; *A.*, 1904, i, 270.
[70] *Ber.*, 1897, **30**, 3020; *A.*, 1898, i, 199. [71] *J.*, 1924, **125**, 2169.

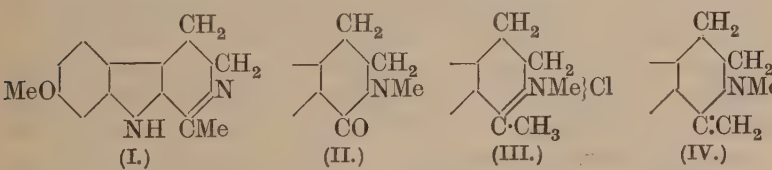
tetracarboxylic acid (due to the loss of the two benzo-groups) which on distillation yielded *apo*harmine (III).



The final operations assumed a microscopic character owing to the destruction of material in the vigorous action necessary in steps II to III, but the production of any *apo*harmine at all illustrates the stability of the heterocyclic nucleus of harmine. The main reaction has been used to build up even more complex derivatives of the harmine type; thus, by condensing diaminoveratrone with benzoylacetone, dibenzoylmethane, etc., derivatives of the general type IV may be built up, and the substance represented by V was obtained from diaminoveratrone and 1 : 3-diketohydrindene.



Although the constitution of harmaline (I) is now known, those of methylharmaline [72] and acetylharmaline are still uncertain.

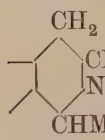


This problem is dealt with by H. Nishikawa, W. H. Perkin, jun., and R. Robinson.[73] Harmaline itself is stable to permanganate in acetone, but the methosulphate and methylharmaline are oxidised to keto-*N*-methyltetrahydronorharmine (II), which is converted

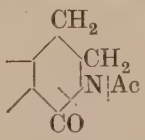
[72] O. Fischer, *Ber.*, 1897, **30**, 2484; *A.*, 1898, i, 164; *ibid.*, 1914, **47**, 102; *A.*, 1914, i, 316.

[73] *J.*, 1924, **125**, 657.

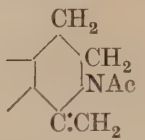
into harmaline methochloride (III) by dilute hydrochloric acid, whence it follows that methylharmaline must have the constitution IV. Acetylharmaline is reduced by hydrogen in presence of palladium to acetyltetrahydroharmine (V) and on oxidation furnishes acetylketotetrahydronorharmine (VI), and must therefore be represented by (VII). On hydrolysis by alcoholic potassium hydroxide, acetylketotetrahydronorharmine (VI) yields 6-methoxy-3-β-aminoethylindole-2-carboxylic acid (VIII) and the corresponding



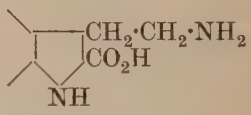
(V.)



(VI.)



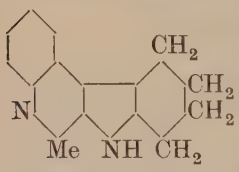
(VII.)



(VIII.)

lactam (analogous with II), but the latter is not convertible into the amino-acid by further action of the hydrolytic agent, and the two substances are doubtless produced simultaneously by hydrolytic fission at the two points shown by dotted lines in VI.

Another interesting synthesis in this series has been described by G. M. Robinson and R. Robinson [74] by way of further experimental evidence against the view [75] that Reddelien's explanation [76] gives the best account of the mechanism of Fischer's indole synthesis, the reaction used being exactly analogous to the latter. 3-Aminoquinaldine was diazotised, the product reduced to 3-hydrazinoquinaldine, and this condensed with *cyclo*hexanone to form 3-methylbenzo-(5 : 6)-9 : 10 : 11 : 12-tetrahydro-4-carboline (annexed formula), which, it will be seen, represents benzotetrahydroharman and a derivative of *apo*harmine (see p. 141).



Y. Asahina [77] has now obtained 3-aminoethylindole by the degradation of evodiamine, thus confirming the modified formula for this alkaloid suggested by Kermack, Perkin, and Robinson.[78]

Eserine.—In last year's Report an account was given of the degradation products of this alkaloid. E. Stedman [79] has now shown that when eserethole methiodide is heated under reduced pressure physostigmol ethyl ether sublimes from it. There were indications that this was an indole derivative and possibly 5-ethoxy-

[74] *J.*, 1924, **125**, 827; compare *ibid.*, 1918, **113**, 639.

[75] C. Hollins, *J. Amer. Chem. Soc.*, 1922, **44**, 1598; *A.*, 1922, i, 863; compare *Ann. Reports*, 1918, **15**, 97; 1922, **19**, 139.

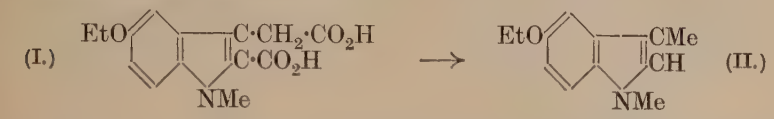
[76] *Annalen*, 1912, **388**, 179; *A.*, 1912, i, 263.

[77] *J. Pharm. Soc. Japan*, 1924, No. 503, 1; *A.*, i, 665.

[78] *J.*, 1921, **119**, 1615; compare *Ann. Reports*, 1921, **18**, 142.

[79] *J.*, 1924, **125**, 1373.

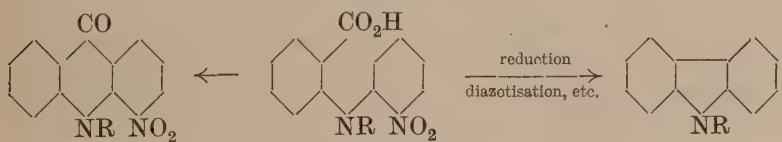
1 : 3-dimethylindole (II), and confirmation of this was obtained by the synthesis of the latter by condensing *p*-ethoxyphenylmethylhydrazine with α-ketoglutaric acid and decarboxylating the 5-ethoxy-2-carboxy-1-methylindole-3-acetic acid (I) formed. This synthesis settles the position of the hydroxyl group in eseroline.



M. and M. Polonovski [80] have shown that eserethole and eserine can behave as secondary bases forming nitroso- and benzoyl-derivatives and on this and other grounds suggest that both bases can exist not only in the tricyclic tertiary base form but also as secondary open-chain bases due to the opening of the reduced pyridine ring, a suggestion already made by G. Barger and E. Stedman [81] to explain the unusual behaviour of eserine on methylation.

Derivatives of Carbazole.

Most of the work done on carbazoles during 1924 is closely associated with that on strychnine and brucine described below and is alluded to there, but a few other interesting observations have been made. H. Burton and C. S. Gibson [82] have described a method for the preparation of 9-alkylcarbazoles, which depends on condensing *N*-alkylanthranilic acids with *o*-bromonitrobenzene to give the corresponding alkyl-2′-nitrodiphenylamine-6-carboxylic acids. These, when heated with sulphuric acid, furnish a small amount of the corresponding 9-nitro-*N*-alkylacridone, and on reduction to the corresponding amino-acids and diazotisation of the latter followed by treatment with sodium hydroxide give good yields of the 9-alkylcarbazoles, which have so far only been obtained by alkylation of carbazole itself.

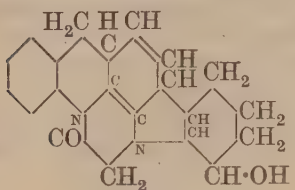


Strychnine and Brucine.

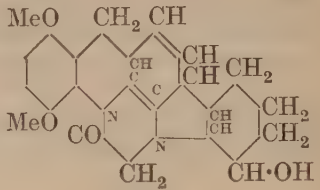
In 1910, W. H. Perkin, jun., and R. Robinson,[83] after a critical

[80] *Compt. rend.*, 1924, **178**, 2078; **179**, 57, 178, 334; *A.*, i, 980, 1093, 1094.
[81] *J.*, 1923, **123**, 760. [82] *J.*, 1924, **125**, 2501.
[83] *J.*, 1910, **97**, 305; compare E. Oliveri-Mandalà, *Gazzetta*, 1924, **54**, 516; *A.*, i, 1101.

review of the experimental data available regarding these two alkaloids, suggested the following formulæ for them in which

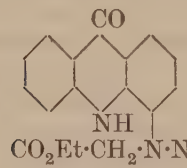


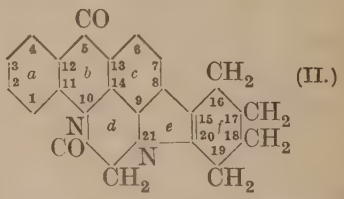
Strychnine.



Brucine.

they are represented as possessing the skeletal system of an anhydro-(5 : 10-dihydro)-acrindoline-21-acetic acid (*see* II *below*). Since then, in spite of much work on the subject, but little progress has been made. G. R. Clemo, W. H. Perkin, jun., and R. Robinson [84] have now given an account of their attempts to build up the structures represented by these formulæ. This has been tried by three methods. It was hoped by reducing nitrosoacridone-9-acetic acid ester (I) with zinc dust in acetic acid in presence of *cyclo*hexanone to produce anhydroketohexahydroacrindolineacetic acid (II), $C_{21}H_{16}O_2N_2$, but the substance actually produced is 5-keto-

(I.) 

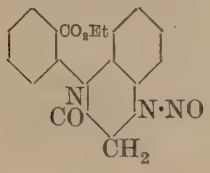
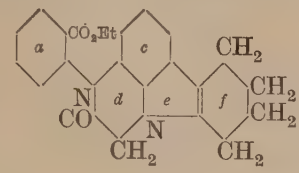
(II.) 

5 : 10 : 16 : 17 : 18 : 19-hexahydroacrindoline, $C_{19}H_{16}ON_2$, which implies the removal of the $-CO-CH_2-$ residue and its replacement by two atoms of hydrogen at positions 10 and 21, so that the double nitrogen ring (*d* in II) is not formed. This elimination of the $-CH_2\cdot CO_2Et$ group may be analogous to the hydrolysis of brucinolic acid to brucinolone and glycollic acid observed by Leuchs and Weber; [85] the reaction has been investigated by W. H. Linnel and W. H. Perkin, jun., for other derivatives of acridine and tetrahydrocarbazole.[86]

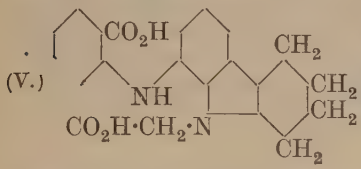
The method was then modified to ensure the formation of ring (*d*) before condensation with *cyclo*hexanone was attempted. 6-Carboxydiphenylamine-2′-acetic acid was esterified, when ring-closure also occurred, producing anhydro-6-carbethoxydiphenylamine-2′-aminoacetic acid, the nitroso-derivative (III) of which

[84] *J.*, 1924, **125**, 1751.
[85] *Ber.*, 1909, **42**, 771; *A.*, 1909, i, 253.
[86] *J.*, 1924, **125**, 2451.

was reduced in presence of *cyclo*hexanone, forming anhydro-8-*o*-carbethoxyphenylaminotetrahydrocarbazole-9-acetic acid (IV).

(III.)  (IV.) 

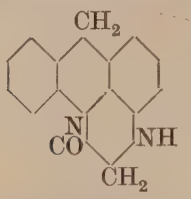
It was now necessary to form ring (*b*) to complete the supposed strychnine skeleton, but although no difficulty was experienced in dehydrating 2′-nitrodiphenylamine-6-carboxylic acid to form 9-nitroacridone (compare p. 143), one of the primary materials used in the first series of experiments, all attempts to effect the corresponding change in IV failed. Thus with sulphuric acid the ester was merely hydrolysed to the acid. Boiling methyl-alcoholic potassium hydroxide opened ring (*d*), producing 8-*o*-carboxyphenylaminotetrahydrocarbazole-9-acetic acid (V), and this was equally insusceptible of the double ring closure, although the lower ring (*d*) could be formed by the action of sulphuric acid, producing anhydrocarboxyphenylaminotetrahydrocarbazoleacetic acid (IV as ester).

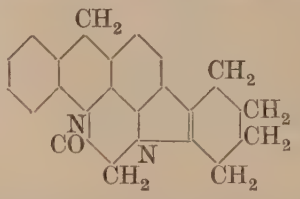
(V.) 

The difficulty of forming the double heterocyclic ring system was thought to be due to the –CO– in the acridone complex, and interest was therefore transferred to the building up of derivatives of dihydroacridine in which $-CH_2-$ replaces –CO–. It was found possible to reduce 9-nitroacridone to 9-amino-5 : 10-dihydroacridine, and the acetyl derivative of the latter, by oxidation followed by hydrolysis gave 9-aminoacridine, from which, by condensation with chloracetic ester, ethyl acridine-9-aminoacetate was produced. The nitroso-derivative of this, however, on reduction in presence of *cyclo*hexanone, gave no carbazole derivative, the nitroso-group being unexpectedly eliminated.

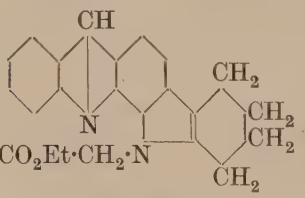
Finally, recourse was had to the method already referred to, formation of indolediazines (p. 139), but although the necessary dimethylacetylaminodihydroacridine was made, it could not be induced to furnish the required dihydroindolediazine. It was then found that chloroacetic ester with 9-amino-5 : 10-dihydroacridine gives anhydro-5 : 10-dihydroacridine-9-aminoacetic acid (VI) directly, and the nitroso-derivative of this, on submission to the usual reaction, condenses to anhydrohexahydroacrindolineacetic acid, $C_{21}H_{18}ON_2$ (VII), which possesses the skeletal system on

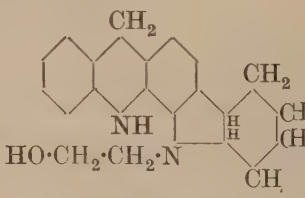
which the formula of strychnine is built up, but differs from strychnine in empirical composition by having one oxygen and four hydrogen atoms less. Like strychnine, it gives in acetic

(VI.) 

 (VII.)

or sulphuric acid solution an intense purple coloration with chromic acid. One striking difference is that on hydrolysis by potassium hydroxide in methyl alcohol, strychnine furnishes strychninic acid (opening of ring *d*), whilst the new substance is partly oxidised, since on again boiling with hydrochloric acid in alcohol there is formed, not only the original substance, but also some ethyl tetrahydroacrindoline-21-acetic acid (VIII); if atmospheric oxidation is allowed to take place freely, this ester is the sole product of the further action of hydrochloric acid in alcohol.

(VIII.) 

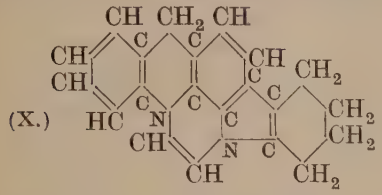
 (IX.)

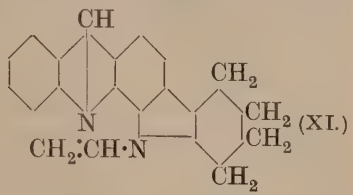
Anhydrohexahydroacrindolineacetic acid (VII) is reduced [87] electrolytically in presence of sulphuric acid in alcohol to 21-hydroxyethyloctahydroacrindoline (IX) by the opening of ring *d*) and reduction of its components $\cdot N{\cdot}CO{\cdot}CH_2{\cdot}N\cdot$ to $\cdot NH$ and $CH_2OH{\cdot}CH_2{\cdot}N\cdot$ just as in the reduction of strychnine to tetrahydrostrychnine, with, however, the difference that in the new substance two hydrogen atoms are added at positions 15 and 20. When distilled with zinc dust, anhydrohexahydroacrindolineacetic acid (VII) is partly converted into 10 : 21-ethano-5 :10 : 16 : 17 : 18 : 20-hexahydroacrindoline, for which formulæ X and XI were considered; the latter was regarded as improbable after examination of the behaviour of *N*-vinyl derivatives of carbazole and tetrahydrocarbazoles with acids,[88] in itself an interesting and complicated piece

[87] For a detailed study of the reduction products of carbazoles and acridines, see W. H. Perkin, jun., and S. G. P. Plant, *J.*, 1921, **119**, 1825; 1923, **123**, 676; 1924, **125**, 1503; *A.*, 1924, i, 1104; and W. H. Perkin, jun., and W. G. Sedgwick, *J.*, 1924, **125**, 2437.

[88] G. R. Clemo and W. H. Perkin, jun., *J.*, 1924, **125**, 1804.

of work, which showed that these substances with warm, dilute sulphuric acid suffered disruption with elimination of the vinyl group and formation of carbazole. The new substance is stable


(X.)


(XI.)

under these conditions and shows the behaviour and properties expected from a dihydroquinoxaline; thus on reduction it adds on four atoms of hydrogen, two in ring (*d*) and two between rings (*e*) and (*f*), becoming 10 : 21-ethano-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-octahydroacrindoline, and this on further reduction (electrolytically) suffers fission of ring (*d*) with the formation of an ethyl side chain at 21 and the addition first of two atoms of hydrogen at 15 and 20 and finally of four more at positions 6, 7, 8, 9.

The formulæ originally proposed for strychnine and brucine (p. 144) were largely based on A. Hanssen's observation [89] that on oxidation with chromic acid strychnine yields carbazole, and although many of the results of previous workers have been confirmed in the course of the present work, it has not been possible to confirm this particular observation, so that the fundamental assumption that strychnine is a carbazole derivative may not be justified.

Derivatives of Glyoxaline.

2-Methylglyoxaline and 4-bromo-2-methylglyoxaline can be sulphonated under the same conditions as glyoxaline itself, and this is in harmony with the view that the sulphonic acid group enters at position 4, although direct proof of this has not been obtained yet.[90] 1-Methylglyoxaline brominates [91] in the same manner as glyoxaline, but the resulting 2 : 4 : 5-tribromo-1-methyl glyoxaline is more resistant to reduction by sodium sulphite than 2 : 4 : 5-tribromoglyoxaline. With methyl sulphate, 4(or 5)-bromoglyoxaline yields both 5-bromo- (51%) and 4-bromo- (1·5%)-1-methylglyoxalines. The latter is better obtained by distilling 4(or 5)-bromo-1 : 3-dimethylglyoxalinium iodide, an observation which negatives J. Sarasin's [92] statement that Wallach's 4(or

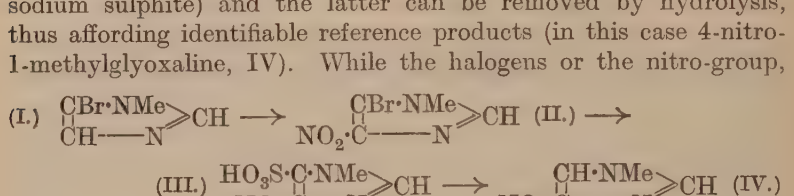
[89] *Ber.*, 1884, **17**, 2849; 1885, **18**, 777; *A.*, 1885, i, 63, 819.

[90] R. Forsyth, J. A. Moore, and F. L. Pyman, *J.*, 1924, **125**, 919; compare *Ann. Reports*, 1920, **17**, 115.

[91] I. E. Balaban and F. L. Pyman, *J.*, 1924, **125**, 1564; compare *Ann. Reports*, 1922, **19**, 143.

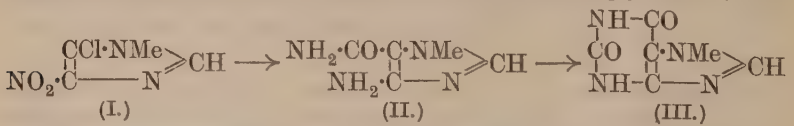
[92] *Helv. Chim. Acta*, 1923, **6**, 370; *A.*, 1924, i, 710.

5)-chloro-1-methylglyoxaline methiodide on distillation yields 5-chloro-1-methylglyoxaline; this correction has since been confirmed.[93] The 4(and 5)-bromo-1-methylglyoxalines (I, Br = 5) are reduced by hydriodic acid and phosphorus, but are unaffected by boiling aqueous sodium sulphite. The reactivity of the halogen is enhanced by the entrance of a nitro-group in the ortho-position to the halogen and in 5-bromo-4-nitroglyoxaline (II) the halogen is replaced by a sulphonic acid group (III) (on boiling with aqueous sodium sulphite) and the latter can be removed by hydrolysis, thus affording identifiable reference products (in this case 4-nitro-1-methylglyoxaline, IV). While the halogens or the nitro-group,



and possibly the –CO– group, in positions 4 (or 5) in glyoxaline favour the formation of alkyl derivatives of the type 5-nitro-1-alkyl on alkylation, methyl, cyanomethyl, and allied groups act in the opposite way and favour the formation of derivatives of the 4 : 1-type. Phenyl as a primary substituent takes an anomalous position; thus 4(or 5)-phenylglyoxaline yields the 4-phenyl-1-methyl and 5-phenyl-1-methyl derivatives in the ratio of 4·8 : 1. On the other hand, the influence of the phenyl group is like that of the nitro-group and the halogens in affecting the products of distillation of the methiodides of 4- and 5-substituted 1-methylglyoxalines, the 4 : 1-substituted glyoxalines being the sole or the dominant product; thus 4(or 5)-phenyl-1 : 3-dimethylglyoxalinium iodide yields 4-phenyl-1-methylglyoxaline with only a small amount of the 5 : 1-isomeride.[94]

J. Sarasin and E. Wegmann[95] record the preparation of heteroxanthine from 5-chloro-4-nitro-1-methylglyoxaline[93] (I). The latter was converted into 5-cyano-4-nitro-1-methylglyoxaline, this



into the corresponding acid, and the 4-amino-amide of this (II) treated with ethyl carbonate, when it yielded heteroxanthine (III).

[93] J. Sarasin and E. Wegmann, *Helv. Chim. Acta*, 1924, **7**, 713; *A.*, i, 1114.

[94] C. E. Hazeldine, F. L. Pyman, and (the late) J. Winchester, *J.*, 1924, **125**, 1431.

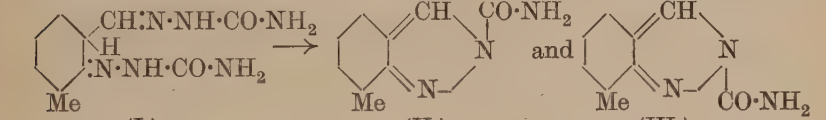
[95] *Helv. Chim. Acta*, 1924, **7**, 713; *A.*, i, 1114; compare R. G. Fargher and F. L. Pyman, *J.*, 1919, **115**, 217.

Benziminazoles.—In 1922, O. Fischer [96] showed that the products formed by the interaction of *o*-aminoazo-compounds with aldehydes and subsequent reduction with hydriodic acid are not triazines as supposed by H. Goldschmidt,[97] but 1-aminobenziminazoles, and a long series of these substances has now been prepared by this means. The action of benzyl chloride on *o*-aminoazo-compounds did not yield the expected *N*-aryldihydrobenziminazoles, but their decomposition products, *e.g.*, aniline and 2-phenylnaphthiminazoles.

Pyrazoles and Indazoles.

Rosenmund's method [98] for the preparation of aldehydes has been successfully applied to a number of pyrazoles.[99] A catalyst was unnecessary, but unless dry, oxygen-free hydrogen was used, acid anhydrides resulted. The pyrazole-3- and -5-aldehydes are oils with the general reactions of aromatic aldehydes. They do not undergo the benzoin or Cannizzaro reactions, the latter affording only traces of the carboxylic acid with resinous by-products as in the case of pyrrole-aldehydes.[1]

Reference was made two years ago in these Reports [2] to some of the problems confronting the worker on indazole derivatives. Auwers and his colleagues have now made a further study of the tetrahydroindazoles,[3] acylindazoles,[4] and alkylindazoles.[5] Excess of semicarbazide converts methylhydroxymethylene*cyclo*hexanone into the disemicarbazone (I) which, in hot dilute sulphuric acid, yields a mixture of the interconvertible labile and stable forms of



(I.) (II.) (III.)

7-methyltetrahydroindazolecarbonamide (II) and (III), which are regarded as stereoisomerides. From these carbonamides the

[96] O. Fischer and others, *J. pr. Chem.*, 1922, [ii], **104**, 102; *A.*, 1922, i, 956; *ibid.*, 1924, [ii], **107**, 16; *A.*, 1924, i, 559.

[97] *Ber.*, 1890, **23**, 487; 1891, **24**, 1000; *A.*, 1890, 614; 1891, 839.

[98] K. W. Rosenmund and others, *Ber.*, 1918, **51**, 585; *A.*, 1918, i, 300; *ibid.*, 1921, **54**, [*B*], 425; *A.*, 1921, ii, 320.

[99] C. A. Rojahn and others, *Annalen*, 1923, **434**, 252; 1924, **437**, 297; *A.*, 1924, i, 91, 875.

[1] H. Fischer and W. Zerweck, *Ber.*, 1923, **56**, [*B*], 519; *A.*, 1923, i, 364.

[2] *Ann. Reports*, 1922, **19**, 132.

[3] K. von Auwers and others, *Annalen*, 1924, **435**, 277; *A.*, i, 325.

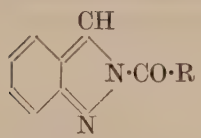
[4] *Ibid.*, 1924, **438**, 1; *A.*, i, 878; *Ber.*, 1924, **57**, [*B*], 1723; *A.*, i, 1348; compare J. Meisenheimer and A. Diedrich, *Ber.*, 1924, **57**, [*B*], 1715; *A.*, i, 1347.

[5] *Ber.*, 1924, **57**, [*B*], 1098.

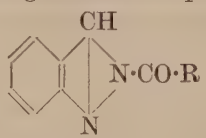
tetrahydroindazoles are obtained by boiling with mineral acids. With phenylhydrazine, on the contrary, a mixture of the non-interconvertible 1- and 2-phenyltetrahydroindazoles is formed, the relative proportion in which 1- and 2-substituted derivatives are formed being dependent on (*a*) the concentration of the hydrion, (*b*) temperature of reaction, (*c*) the nature of the hydrazine derivative—phenyl, phenylmethyl, benzyl, and so on.

On alkylation, 1- or 2-alkyl-substituted tetrahydroindazoles, or both, are formed depending partly on the nature of the alkyl group and partly on the experimental conditions, but methyl in position 7 inhibits alkylation in position 1.

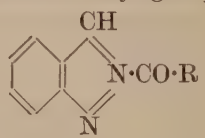
As the result of a detailed study of the relative stabilities of the labile forms of the acylindazoles and a comparison of their physical properties with those of the stable forms, three formulæ have been put forward by Auwers and Allardt [4] for acylindazoles, of which III is regarded as unlikely, II is considered probable for both forms from the results of spectrochemical examination, whilst I may be necessary to explain the colour of some of the labile isomerides. The isomerism is regarded as steric, which introduces a difficulty with regard to II, since isomerism in this case involves considerable strain. Formula I has the further advantage that hydrogen chloride should add on in position 1 with difficulty in the case of one isomeride owing to the proximity of the acyl group, and this does occur, hydrogen chloride splitting off the acyl group.



(I.)



(II.)



(III.)

It has, however, been pointed out [6] that formula I is not compatible with the assumption, previously made, [3] that stereoisomerism in this group is due to the presence of an asymmetric tervalent nitrogen atom. The only other possible explanation (position 3 being impossible in view of new experimental evidence) is that one of the forms contains the acyl group in position 1, a possibility already considered but rejected by Auwers on the ground that "1-acetylindazole" obtained from *o*-aminobenzaldoxime is not identical with either the labile or stable form of acetylindazole now under discussion. Re-examination of this "1-acetylindazole" indicates, however, that it is really 4 : 5-benzo-7-methylhept-1 : 2 : 6-oxadiazine, $C_6H_4<\begin{matrix}C(OH):N\\N=CMe\end{matrix}>O$.

[6] J. Meisenheimer and A. Diedrich, *Ber.*, 1924, **57**, [*B*], 1715; *A.*, i, 1347; compare K. von Auwers, *ibid.*, p. 1723; *A.*, i, 1348.

T. A. Henry.

ANALYTICAL CHEMISTRY.

The story of a year's progress in analytical chemistry must of necessity be somewhat disconnected, for analysis is not an end in itself, but only the chief means by which the aims of all the other branches of chemistry are attained. Hence, a report, if it is to be of general use for the purpose of reference, must cover a very wide ground and be classified in such a way as to show rapidly which of the new methods outlined are likely to be applicable for special purposes. As space is no longer available for the inclusion of all the modifications of methods devised during the preceding year, it has been found necessary to make the selection mainly from those processes in which new principles have been applied, or in which a more trustworthy procedure has been described.

Physical Methods.

It has been ascertained that the rate of diffusion of fatty acids in alcohol through a collodion membrane decreases with the increase in the molecular weight of the fatty acids, and this principle has been adapted to the detection and separation of mixtures of acids, such as stearic and lauric acids.[1]

Various forms of apparatus for filtration through membranes (ultra-filtration) have been devised, the filter being made of porous earthenware coated on the inside with a layer of collodion,[2] or of unglazed porcelain or cellulose acetate.[3] These filters are suitable for the separation of electrolytes from colloidal solutions, and for the filtration of colloidal silver, hæmoglobin, etc.

A method of detecting the presence of a mixture of constant boiling point consists in fractional distillation at a different pressure until a sufficient quantity of the constituents has been separated to leave a mixture of constant boiling point with a different composition.[4]

A rapid method of determining sulphur in the form of a soluble sulphate depends upon its titration with barium chloride solution in a Dewar vacuum tube, measurement of the temperature at intervals, and plotting the readings against the volume of barium

[1] A. Heiduschka and J. Ripper, *Z. Elektrochem.*, 1923, **29**, 552; *A.*, ii, 73

[2] H. Bechhold and L. Gutlohn, *Z. angew. Chem.*, 1924, **37**, 494; *A.*, ii, 621.

[3] L. Zakarias, *ibid.*, 425; *A.*, ii, 622.

[4] T. R. Briggs, *J. Physical Chem.*, 1924, **28**, 644; *A.*, ii, 776.

chloride solution. The end-point is indicated by a break in the curve.[5]

As usual, the principal contributions to this branch of analytical chemistry have been extensions of optical methods. A spectrophotometric method of determining hydrogen-ion concentration has been based upon the observation that the wave-lengths of the absorption bands in a solution containing an indicator are not altered by a change in the hydrogen-ion concentration, but that the intensity of absorption (height) of the bands is changed and can be measured and compared with that in a buffer solution containing the same indicator.[6] Another spectrophotometric method consists in determining the degree of colour transformation of an indicator, which, in the case of two-colour indicators, may be obtained from the ratio of the intensities of absorption at two wave-lengths near the maxima of the respective absorption bands.[7]

Methods for the identification of phenols, especially in medicinal preparations, have also been devised,[8] and tables have been constructed showing the relationship between the concentration of solutions of arabinose or xylose and the extinction coefficient of the band of maximum absorption given in amyl alcohol solution by the blue pigment formed on treating these pentoses with Bial's orcinol reagent.[9]

Mention may also be made of the use of colloidal poles of gelose (from agar-agar) for observing the emission spectra of dilute solutions and their application to the detection of metals.[10]

Further work has been done on the application of fluorescence phenomena as a means of identifying a number of organic compounds, such as quinol, pyrocatechol, and salicylic acid. The substance is exposed to ultra-violet light from a mercury vapour lamp.[11]

A new optical method of determining starch consists in treating two portions of a mixture of starch and water with diastase, one with and the other without gelatinisation by heat, filtering the two liquids, and comparing the filtrates in the interferometer. The results are somewhat lower than those obtained by chemical methods.[12]

[5] P. M. Dean and O. O. Watts, *J. Amer. Chem. Soc.*, 1924, **46**, 855; *A.*, ii, 421. Compare *Ann. Report*, 1922, **19**, 166.
[6] W. R. Brodie, *ibid.*, 581; *A.*, ii, 346.
[7] W. C. Holmes, *ibid.*, 627; *A.*, ii, 346.
[8] S. Palkin and H. Wales, *ibid.*, 1488; *A.*, ii, 630.
[9] G. Scheef, *Biochem. Z.*, 1924, **147**, 94; *A.*, ii, 632.
[10] J. Errera, *Bull. Soc. chim. Belg.*, 1924, **33**, 449; *A.*, ii, 802.
[11] E. Bayle and R. Fabre, *J. Pharm. Chim.*, 1924, **29**, 535.
[12] O. Wolff, *Z. angew. Chem.*, 1924, **37**, 206; *A.*, ii, 506.

There have been several contributions to the methods of using the *X*-ray spectrum in qualitative and quantitative analysis, and it has been shown that, when a sufficiently long exposure to the photographic film is given, as little as 1% of an element in 1 mg. of a mixture can thus be detected.[13] For quantitative work the substance may be imbedded in an indifferent material such as graphite, together with a standard substance, and the ratio between the intensities of the lines of the two substances is then determined. The method is only applicable, however, to solid elements heavier than sodium.[14]

Gas Analysis.

Among the new forms of apparatus devised for the analysis of gases is a spiral washing bottle which insures intimate contact between the gas and the liquid, and so promotes the absorption.[15] A device of a similar type has been used for separating hydrogen peroxide vapour from ozone, the mixture being passed through a spiral chilled in a mixture of ether and solid carbon dioxide, with the result that only the peroxide is condensed. Alternatively, by passing the gaseous mixture through dilute acidified permanganate solution, the peroxide is destroyed, and the ozone can be determined by absorption in potassium iodide solution.[16]

For the analysis of mixtures of nitric oxide and nitrogen peroxide the gas is shaken with concentrated sulphuric acid, which absorbs equal moleuclar proportions of each gas, forming nitrogen trioxide, the amount of which is determined by means of the nitrometer. The excess of nitric oxide in the residual gas is determined by means of the nitrometer after oxidation of both gases with potassium bromate.[17]

An investigation of various absorbents for carbon monoxide has shown that the most efficient is a mixture of cuprous chloride, fine pumice, and powdered soda-lime.[18] The compound of cuprous sulphate and ethylene described by Damiens,[19] forms, when suspended in sulphuric acid, a good absorbent for carbon monoxide, but it also absorbs oxygen, ethylene, and acetylene, which must therefore be removed before the absorption.[20] These three gases are absorbed less readily by another new reagent for carbon monoxide prepared by shaking a suspension of cuprous oxide in sulphuric acid for

[13] D. Coster, *Chem. Weekblad*, 1924, **21**, 59; *A.*, ii, 199.
[14] H. Stintzing, *Z. physikal. Chem.*, 1924, **108**, 58; *A.*, ii, 216.
[15] L. H. Milligan, *Ind. Eng. Chem.*, 1924, **16**, 889; *A.*, ii, 776.
[16] M. Bamberger and K. Trautzl, *Z. anal. Chem.*, 1924, **64**, 9; *A.*, ii, 563.
[17] A. Klemenc and K. Mula, *Z. anorg. Chem.*, 1924, **134**, 208; *A.*, ii, 498.
[18] A. Piutti, *Rend. Accad. Fis. Mat. Napoli*, 1922, **28**, 91; *A.*, ii, 59.
[19] A. Damiens, *A.*, 1921, i, 1105.
[20] *Idem, Compt. rend.*, 1924, **178**, 849; *A.*, ii, 567.

several hours with a phenolic substance, such as β-naphthol, and filtering the solution.[21]

A method of determining carbonyl chloride in gas mixtures containing hydrogen chloride and carbon dioxide consists in shaking the gas with water to absorb the hydrogen chloride, and then with a measured excess of standard potassium hydroxide solution (which absorbs both carbon dioxide and carbonyl chloride), and finally determining the carbonyl chloride by adding excess of hydrochloric acid and titrating the excess with standard barium hydroxide solution. The reaction upon which the method is based is

$$COCl_2+4KOH=2KCl+K_2CO_3+2H_2O.$$[22]

In determining organic vapours, such as benzene, by adsorption with active charcoal it is necessary to take into account the fact that the charcoal at first retains a large proportion of benzene after steaming at 130°, but that afterwards this loss becomes constant, and an average of 99·6 % is then expelled by the steam.[23] The most satisfactory results are obtained when the steaming of the charcoal is carried out in the same U-tube in which the benzene was adsorbed.[24]

Agricultural Analysis.

A new method of determining humic matter in soils depends upon a colorimetric comparison of the hydrochloric acid extract of the soil, after treatment with excess of alkali, with a standard solution of Acidum Huminicum (Merck) under parallel conditions.[25]

The adsorptive method of determining colloidal matter in soils has been shown to give results which, with the application of a correction, agree closely with those obtained by microscopical examination.[26] The percentage of colloidal matter is expressed in terms of the ratio of the adsorption per g. of the soil to that of the extracted colloids, multiplied by 100.[27]

The difficulty of obtaining a clear solution of soil for the colorimetric determination of the hydrogen-ion concentration may be overcome by dialysing the mixture of soil and water for 24 hours through a porous membrane. The results then obtained were found to be more accurate than those given by the electrometric method.[28]

[21] P. Lebeau and C. Bedel, *Compt. rend.*, 1924, **179**, 108; *A.*, ii, 627.

[22] G. Bredig and A. von Goldenberg, *Gas-u. Wasserfach.*, 1924, **67**, 490; *A.*, ii, 701.

[23] E. Berl and E. Wachendorff, *Z. angew. Chem.*, 1924, **37**, 205; *A.*, ii, 505.

[24] F. Fischer and C. Zerbe, *ibid.*, 483; *A.*, ii, 630.

[25] T. Eden, *J. Agric. Sci.*, 1924, **14**, 469; *A.*, ii, 796.

[26] Compare *Ann. Report*, 1923, **20**, 160.

[27] P. L. Gile and others, *U.S. Dept. Agric. Bull.*, 1924, 1193; *A.*, ii, 796.

[28] I. M. Kolthoff, *Chem. Weekblad*, 1923, **20**, 675; *A.*, ii, 199. Compare *Ann. Report*, 1923, **20**, 161.

On the other hand, comparative determinations by the electrometric method and by a colorimetric method (with the use of methyl-red, bromophenol-blue, bromocresol-purple, and methyl-red), in which the aqueous suspensions of the soil were separated centrifugally, gave results differing by not more than 0·19 p_H.[29]

Notwithstanding criticisms of the untrustworthiness of "citric solubility" as a criterion of the fertilising power of mineral phosphates,[30] evidence of the difference in the behaviour of various natural phosphates in the test has once more been put forward, and it is claimed that the ratio of the amount of phosphoric acid soluble in 2% citric acid solution to that of the total phosphoric acid affords a measure of the fertility of a soil.[31] A potentiometric method of determining this "citric acid ratio" has been devised.[32]

One difficulty in the way of obtaining accurate results in the phenoldisulphonic acid method of determining nitrates is the adsorption of nitrate by the filter-paper [33] or by animal charcoal. This may be largely overcome by precipitating copper hydroxide from calcium hydroxide and copper sulphate in the soil suspension, the extract being thereby decolorised without losing more than traces of nitrate.[34]

Organic Analysis.

Qualitative.—It has been shown that a solution of magenta and sulphurous acid (Schiff's reagent) will give a coloration with undiluted ethyl alcohol, but not with dilute (5—10%) alcohol. The test will detect 0·00005 c.c. of 37% formaldeyhde in 5 c.c. of dilute alcohol. A still more sensitive test for formaldehyde depends upon the purple coloration obtained with morphine sulphate and sulphuric acid.[35] Both formaldehyde and acetaldehyde give a white precipitate with Bial's reagent (orcinol, ferric chloride and hydrochloric acid), but the two precipitates may be distinguished by their behaviour on heating and on the addition of alkali.[36] A microchemical method capable of detecting 0·001 mg. of acetaldehyde in fruits has been based on the formation of characteristic crystals of acetaldehyde-*p*-nitrophenylhydrazone, but the test is not dis-

[29] R. M. Barnette, F. C. Gerretsen, D. J. Hissiak, and J. van der Spek, *Chem. Weekblad*, 1924, **21**, 145; *A.*, ii, 347.

[30] Compare *Ann. Report*, 1922, **19**, 169.

[31] G. André and H. Copaux, *Bull. Soc. chim.*, 1924, [iv], **35**, 1113; *A.*, ii, 871.

[32] H. Copaux and J. Daric, *ibid.*, 1115; *A.*, ii, 872.

[33] Compare *Ann. Report*, 1923, **20**, 161.

[34] H. J. Harper, *Ind. Eng. Chem.*, 1924, **16**, 180; *A.*, ii, 274.

[35] J. L. Mayer, *J. Amer. Pharm. Assoc.*, 1923, **12**, 698; *A.*, ii, 210.

[36] J. B. Sumner, *J. Amer. Chem. Soc.*, 1923, **45**, 2378; *A.*, ii, 70.

tinctive, since other aldehydes and ketones yield analogous crystalline compounds.[37]

An alcoholic solution of vanillin can replace salicylaldehyde as a reagent for acetone; it produces a red ring above acetone to which a fragment of solid sodium hydroxide has been added.[38] Both acetone and acetoacetic acid give a coloration with sodium nitroprusside, but only acetoacetic acid gives a colour reaction with ferric chloride.[39]

A useful test for chloroform and chloral hydrate in amounts up to 0·005 mg. has been based upon the fact that compounds containing the group CX_3 (in which X represents a halogen) give a red coloration when heated with sodium hydroxide solution and pyridine.[40]

The ferrous tartrate test for tannins and their derivatives [41] is not specific for tannins, but a solution of a mixture of neutral iron ammonium citrate and ammonium citrate apparently gives a precipitate only with tannin and not with gallic acid or phlobotannin.[42] A sensitive modification of the gold-beater's skin test for tannins [43] has been devised, and it has been shown that subsequent treatment of the stained skin with hydrochloric acid enables phlobaphens to be distinguished from tannins.[44] Osmium tetroxide can be used as a reagent in the test, but is less sensitive than ferrous sulphate.[45]

A reagent that will distinguish resorcinol from other phenols consists of a mixture of sodium nitroprusside, sodium acetate and ammonia solutions; it gives with resorcinol a blue-green coloration, changing to yellow on the addition of excess of sodium hydroxide.[46]

The reaction with Hofmann's-violet decolorised with sulphuric acid, which was put forward by Guareschi as specific for proteins, has been shown to be produced by nitrogenous compounds in general of slight acidity or alkalinity.[47]

Quantitative.—Several contributions have been made to the methods for the ultimate analysis of organic compounds. In the case of volatile compounds, a convenient method is to conduct the vapour into the combustion tube by means of a current of warm

[37] C. Griebel, *Z. Unters. Nahr. Genussm.*, 1924, **47**, 438; *A.*, ii, 791.
[38] H. Leffmann, *Amer. J. Pharm.*, 1924, **96**, 507; *A.*, ii, 791.
[39] E. J. Bigwood and W. L. Ladd, *J. Biol. Chem.*, 1923, **58**, 347; *A.*, ii, 210.
[40] J. H. Ross, *ibid.*, 1923, **58**, 641; *A.*, ii, 352.
[41] Compare *Ann. Report*, 1923, **20**, 165.
[42] A. H. Ware, *Analyst*, 1924, **49**, 467; *A.*, ii, 789.
[43] E. Atkinson and E. O. Hazelton, *Biochem. J.*, 1922, **16**, 516; *A.*, 1922, ii, 793.
[44] P. H. Price, *Analyst*, 1924, **49**, 25; *A.*, ii, 209.
[45] *Idem*, *ibid.*, 336; *A.*, ii, 574.
[46] Cazeneuve, *Ann. Chim. Analyt.*, 1924, [ii], **6**, 43; *A.*, ii, 356.
[47] G. Lo Priore, *Chem. Zentr.*, 1924, i, 947; *A.*, ii, 795.

oxygen.[48] For determining carbon by the wet method, the substance may be heated with an excess of potassium persulphate in aqueous solution, and the carbon dioxide dried and weighed.[49] Another rapid method is to oxidise the organic substance by means of permanganic anhydride in sulphuric acid, and to determine volumetrically the carbon dioxide produced.[50] The wet method has also been made applicable to nitrogen, the substance being digested with sulphuric acid and potassium dichromate, and the nitrogen determined as in the Kjeldahl process. Chlorides must be removed in the form of hydrogen chloride by aëration prior to the addition of the dichromate, or the results will be too low.[51] This oxidation method with dichromate has also been adapted to micro-determination of carbon and nitrogen.[52]

The method of determining halogens by combustion in a current of oxygen over platinised asbestos and absorption of the halogen by silver powder has been claimed to give good results with nitrogenous substances, notwithstanding statements to the contrary. If sulphur also is present, the products of combustion are made to pass over sodium carbonate at 400—500°, and halogen is determined in one portion and sulphur in the other.[53] A new method consists in heating the organic substance in a current of a mixture of hydrogen and ammonia, and determining the halogen volumetrically in the ammonium halide produced.[54] Or the combustion may be carried out in a current of oxygen in the presence of, but not in contact with, ferric chloride, and the products led into an alkali sulphide solution, which is afterwards acidified and the halogen titrated.[55] Fluorine may be determined by heating the substance with potassium at 400°, and titrating the potassium fluoride conductometrically with calcium chloride.[56]

Magnesium perchlorate trihydrate is recommended as a readily-prepared and stable substitute for calcium chloride as an absorbent in organic analysis, as well as for phosphoric oxide in the analysis of steel by combustion.[57]

[48] M. E. Carrière and C. Leenhardt, *Bull. Soc. chim.*, 1924, [iv], **35**, 1206; *A.*, ii, 869.

[49] A. Franz and H. Lutze, *Ber.*, 1924, **57**, [*B*], 768; *A.*, ii, 500.

[50] J. F. Durand, *Compt. rend.*, 1924, **178**, 1193; *A.*, ii, 500.

[51] A. K. Anderson and H. S. Schutte, *J. Biol. Chem.*, 1924, **61**, 57; *A.*, ii, 699.

[52] H. Dieterle, *Arch. Pharm.*, 1924, **262**, 35; *A.*, ii, 567.

[53] F. Arndt, *Ber.*, 1924, **57**, [*B*], 763; *A.*, ii, 497.

[54] H. ter Meulen and J. Heslinga, *Rec. trav. chim.*, 1923, **42**, 1093; *A.*, ii, 55.

[55] J. Heslinga, *ibid.*, 1924, **43**, 181; *A.*, ii, 419.

[56] J. Piccard and C. Buffat, *Helv. Chim. Acta*, 1923, **6**, 1047; *A.*, ii, 122.

[57] G. F. Smith, M. Brown, and J. F. Ross, *Ind. Eng. Chem.*, 1924, **16**, 20; *A.*, ii, 198.

It has been shown that amino- and carboxyl groups in amino-acids, etc., can be determined by a series of titrations to different p_H values, the point to which the neutralisation is to be carried being found by reference to the titration curves of the acid in question.[58] In titrating the amino-group, the solution is neutralised to phenolphthalein, and then titrated with hydrochloric acid, with methyl-red as indicator. In the case of arginine, the carboxyl group and one of the amino-groups do not react.[59] The methods of acidimetry appear to be practicable, not only with amino-acids, but also with albumin, gliadin, casein, and gelatin, and the curves obtained with the products of hydrolysis of these proteins indicate that the original substances may thus be characterised.[60]

A modification of the dichromate method of determining glycerol has been deivsed, and has shown that the curd fibres of sodium palmitate adsorb glycerol negatively at the ordinary temperature, even in the absence of salt.[61]

Among the few new contributions to analytical methods for oils and fats are two methods for determining the acetyl value : one by determining the increase in weight after acetylation, and the other by using chloroacetyl chloride for the acetylation, and calculating the acetyl value from the amount of chlorine used, this being determined volumetrically.[62] It has been shown that linseed oil, on bromination, yields two crystalline bromides of mixed glycerides, and a method of examining linseed oil has been based on the determination of the bromide more insoluble in ethyl acetate.[63] One of these bromides has been prepared independently, and its composition as the bromide of α-dilinolenin-α-linolin has been confirmed.[64]

Tartaric acid may be determined by oxidising it with potassium iodate and sulphuric acid :

$$C_4H_6O_6 + 2KIO_3 + H_2SO_4 = K_2SO_4 + I_2 + 4CO_2 + 4H_2O.$$

The liberated iodine is expelled by boiling, and the excess of iodate is determined iodometrically.[65]

It has been found that the ferrocyanides of sodium, potassium, or calcium yield an insoluble white precipitate of benzidine hydroferrocyanide, $(C_{12}H_{12}N_2)_3,H_4Fe(CN)_6$, on treatment with a benzidine

[58] L. J. Harris, *Proc. Roy. Soc.*, 1923, [*B*], **95**, 440; *A.*, ii, 75.
[59] *Idem, ibid.*, 1924, [*B*], **95**, 500; *A.*, ii, 355.
[60] P. Hirsch, *Biochem. Z.*, 1924, **147**, 433; *A.*, ii, 795.
[61] H. B. Bennett, J., 1924, **125**, 1971.
[62] R. Biazzo, *Chem. Zentr.*, 1924, i, 2030; *A.*, ii, 708.
[63] H. Toms, *Analyst*, 1924, **49**, 77; *A.*, i, 365.
[64] A. Eibner and K. Schmidinger, *Chem. Umschau*, 1923, **30**, 293; *A.*, ii, 131.
[65] R. Strebinger and J. Wolfram, *Oesterr. Chem. Ztg.*, 1923, **26**, 156; *A.*, ii, 73.

salt, and that this reaction can be used for determining ferrocyanides either gravimetrically by determination of the iron or volumetrically with the use of sodium hypobromite as an outside indicator.[66]

An attempt has been made to extend Mitchell's ferrous tartrate method of determining the pyrogallol tannins [67] to the pyrocatechol tannins, and it has been found that, whilst good results could be obtained in comparing pyrocatechol, protocatechuic acid, and catechins by themselves, the method failed when used for comparing them with one another. It was also established that the formation of a violet coloration with the reagent depends upon the presence of two hydroxyl groups in the ortho-position.[68] It was afterwards shown that by suitable adjustment of the hydrogen-ion concentration of the tannin solution the method is also applicable to the pyrocatechol tannins, the apparent failure with them being due to the fact that they differ more widely than the pyrogallol tannins in the p_H values at which their maximum intensity of colour is given.[69] It has also been found that osmium tetroxide can be used for the colorimetric determination of both groups of tannins.[70] The ferrous tartrate colorimetric method has been shown to give trustworthy results in determining the amount of gallic acid produced in the hydrolysis of gallotannin by tannase.[71]

For determining tannin in plant-tissue, a colorimetric method has been devised in which the reagent is prepared by boiling together sodium tungstate, arsenic acid (As_2O_5), and hydrochloric acid. A solution of pure gallotannin (freed from gallic acid) is used as the standard for the colorimetric comparison,[72] and therein lies the weak point of the method, for "pure" gallotannin may contain variable proportions of glucose or practically none.[73]

A modification of the colorimetric method of determining sugars by means of picric acid has been applied to the determination of carbohydrates in plants, and has been shown to give more accurate results with small amounts of reducing sugars and sucrose than either the volumetric or the reducing method.[74] Starch can also be determined by the same method after hydrolysis to dextrose

[66] W. J. Cumming, J., 1924, **125**, 240.
[67] C. A. Mitchell, *Analyst*, 1923, **48**, 1; *A.*, 1923, ii, 188.
[68] P. H. Price, *ibid.*, 1924, **49**, 361; *A.*, ii, 707.
[69] S. Glasstone, *Soc. Public Analysts*, Dec. 5, 1924.
[70] C. A. Mitchell, *Analyst*, 1924, **49**, 162; *A.*, ii, 356.
[71] W. N. Nicholson and D. Rhind, *ibid.*, 505; *A.*, ii, 875.
[72] P. Menaul, *J. Agric. Res.*, 1923, **26**, 257; *A.*, ii, 360.
[73] Compare *Ann. Report*, 1923, **20**, 166.
[74] W. Thomas and R. A. Dutcher, *J. Amer. Chem. Soc.*, 1924, **46**, 1662; *A.*, ii, 630.

and maltose by means of taka-diastase;[75] or fresh malt solution may be used for the hydrolysis.[76] As a standard for comparison in this method, the use of a 0·08% solution of dextrose or a 0·076% solution of sucrose in saturated picric acid solution is suggested. The intensity of coloration is not proportional to the dilution, and it is therefore necessary to dilute by a standardised method. Correction factors are also required, since the degree of coloration is not proportional to the amount of sugar.[77]

It has been shown that under definite conditions for time, temperature, and proportions of iodine and alkali the iodometric method gives quantitative results in the oxidation of dextrose, lactose, sucrose, and lævulose.[78] An iodometric method has also been devised for determining the nitrogen in osazones.[79] By heating dextrose with an excess of phenylhydrazine in acetic acid, it is quantitatively converted into its osazone, which may be determined by reduction with titanous chloride and titration of the excess of this with crystal-scarlet. The method is also applicable to other carbohydrates yielding osazones under the same conditions.[80]

The polarimetric constants of lactose have been redetermined and a formula for its determination has been devised,[81] and a polarimetric method of determining raffinose in sugars worked out.[82] Determination of sugar in urine by means of Fehling's solution, with methylene-blue as internal indicator, has been shown to give more accurate results than Pavy's method.[83]

The furfuraldehyde yielded by pentoses and pentosans may be accurately determined in acid solution by the use of potassium bromate in the presence of potassium bromide.[84] A colorimetric method, accurate to $\pm 2{\cdot}5\%$, has also been devised; it depends upon the coloration given by furfuraldehyde with aniline and acetic acid.[85]

A method for determining lignin has been based on its insolu-

[75] W. Thomas, *J. Amer. Chem. Soc.*, 1924, **46**, 1670; *A.*, ii, 635.

[76] M. R. Coe and G. L. Bidwell, *J. Assoc. Off. Agric. Chem.*, 1924, **7**, 297; *A.*, ii, 429.

[77] J. Willaman and F. R. Davison, *J. Agric. Res.*, 1924, **28**, 479; *A.*, ii, 789.

[78] C. L. Hinton and T. Macara, *Analyst*, 1924, **49**, 2; *A.*, ii, 209.

[79] D. R. Nanji, *Biochem. J.*, 1923, **17**, 761; *A.*, ii, 209.

[80] E. Knecht and E. Hibbert, J., 1924, **125**, 2009.

[81] A. L. Bacharach, *Analyst*, 1923, **48**, 521; *A.*, ii, 72.

[82] E. Saillard, *Compt. rend.*, 1924, **178**, 2189; *A.*, ii, 632.

[83] J. H. Lane and L. Eynon, *Analyst*, 1924, **49**, 366; *A.*, ii, 707.

[84] N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.*, 1924, **15**, 1255; *A.*, ii, 71.

[85] G. E. Youngburg and G. W. Pucker, *J. Biol. Chem.*, 1924, **61**, 741; *A.*, ii, 876.

bility in a solution of phosphorus pentoxide in hydrochloric acid, which will dissolve wood cellulose.[86]

The fact that pyridine is quantitatively precipitated by silicotungstic acid has been made the basis of a method for its determination, especially in the presence of nicotine.[87]

It has been proved that the red coloration in Jaffe's reaction for determining creatinine is due to the formation of a red tautomeride of creatinine picrate.[88]

A colorimetric method of determining adrenaline depends upon its forming a red coloration when treated successively with sulphanilic acid, nitrous acid, and ammonia.[89]

Mention may also be made of a colorimetric method of determining diastase, which consists in digesting the enzyme solution with excess of erythrodextrin, determining the unaltered dextrin by adding iodine solution and ammonium sulphate, and comparing the colour with a standard.[90]

Inorganic Analysis.

Qualitative.—All the common heavy metals form pyridine–thiocyanate compounds, with the general formula $M(CNS)_2,(C_5H_5N)_2$,[91] and some metals form analogous compounds with antipyrine (cadmium) and pyramidone (copper).[92] The pyridine–thiocyanate compounds of zinc and cadmium form distinctive crystals, by which they can be identified.[93] Diphenylcarbazide can also be used as a specific reagent for certain metals (mercury, copper, cadmium, and magnesium) by varying the conditions in each case, *e.g.*, by adding halogen salts.[94]

The use of cæsium chloride as a general microchemical reagent has been developed, a large number of metals forming characteristic double chlorides with it.[95] Other useful microchemical reagents include pyrogallol for tervalent antimony, benzoinoxime for copper, and benzidine for manganese and phosphoric acid.[96] Potassium, ammonium, and magnesium may be distinguished by the different forms of the crystals they yield on treatment with sodium benzenesulphonate.[97]

[86] H. Wenzl, *Papierfabr.*, 1924, **22**, 101; *A.*, ii, 429.
[87] F. Mach and F. Sindlinger, *Z. angew. Chem.*, 1924, **37**, 89; *A.*, ii, 357.
[88] I. Greenwald and J. Gross, *J. Biol. Chem.*, 1924, **59**, 601; *A.*, ii, 508.
[89] H. Friend, *ibid.*, 1923, **57**, 497; *A.*, ii, 75.
[90] I. Cohen and E. C. Dodds, *Brit. Med. J.*, 1924, I, 618; *A.*, ii, 636.
[91] Compare *Ann. Report*, 1923, **20**, 168.
[92] I. M. Kolthoff and H. Hamer, *Pharm. Weekblad*, 1924, **61**, 1222; *A.*, ii, 873.
[93] *Idem*, *Mikrochemie*, 1924, **2**, 92; *A.*, ii, 785.
[94] I. M. Kolthoff, *Chem. Weekblad*, 1924, **21**, 20; *A.*, ii, 124.
[95] E. H. Nicloux, *Mikrochemie*, 1924, **2**, 108; *A.*, ii, 783.
[96] F. Feigl, *Mikrochemie*, 1923, **1**, 74; *A.*, ii, 206.
[97] L. Rosenthaler, *ibid.*, 1924, **2**, 29; *A.*, ii, 782.

Several new tests for individual metals have also been described. Thus, an alcoholic solution of guaiacum resin may be used as a sensitive reagent for copper.[98] That metal also gives a red coloration with an alcoholic solution of aloin and a green coloration with a solution of benzidine.[99]

Stannous chloride will reduce mercuric chloride to metallic mercury in presence of aniline, and tin may thus be detected when present with the other ordinary metals. The same reaction, applied by means of stannous chloride paper, may be used for the detection of mercury.[1] In the absence of copper, ferrous salts give a bluish-green coloration with 2 : 4-dinitroresorcinol, and the colour becomes bright green if ferric salts are present.[2]

A test that will detect 1 part of cobalt in 830,000 parts consists in treating the acid solution with sodium acetate and dimethylglyoxime, filtering off any precipitated nickel, and adding sodium sulphide to the filtrate. A violet coloration, due to the formation of a compound, $[CMe(:NOH)]_2:::Co(\cdots H_2O)(\cdots NH_3):S$, indicates cobalt.[3]

A very sensitive test for nickel depends upon the formation of a red compound, $[CMe(:N\cdot OH)CMe:NO\cdot]_2NiO$, on boiling the solution with concentrated ammonia, lead dioxide, a few drops of sodium hydroxide solution, and alcoholic dimethylglyoxime. The filtrate will vary from dark red to reddish-yellow, according to the quantity of nickel present.[4] Another test for nickel and cobalt consists in adding an excess of sodium hydrogen carbonate, followed by a few drops of bromine water, to the solution. A green coloration indicates nickel, and the precipitate turns black on heating if cobalt is present.[5]

Thiocarbamide and hydrochloric acid give a blue-green coloration with ruthenium. Osmium also gives a coloration with the reagent, but may be distinguished by its forming a red solution on the addition of thiocarbanilide.[6]

Several new colour reactions of zirconium have been described. One is that zirconium yields coloured complex salts with β-naphthol or β-nitroso-α-naphthol;[7] another consists in the production of a reddish-violet coloration (not discharged by excess of hydrochloric

[98] R. Fleming, *Analyst*, 1924, **49**, 275; *A.*, ii, 500.
[99] L. Rosenthaler, *Mikrochemie*, 1924, **2**, 121; *A.*, ii, 785.
[1] N. A. Tannaer, *Z. anorg. Chem.*, 1924, **133**, 372; *A.*, ii, 571.
[2] M. Goldstück, *Chem. Ztg.*, 1924, **48**, 629; *A.*, ii, 703.
[3] F. Feigl and L. von Tustanowska, *Ber.*, 1924, **57**, [*B*], 762; *A.*, ii, 504.
[4] F. Feigl, *ibid.*, 758; *A.*, ii, 504.
[5] C. C. Palit, *Chem. News*, 1924, **128**, 293; *A.*, ii, 426.
[6] L. Wöhler and L. Metz, *Z. anorg. Chem.*, 1924, **138**, 368; *A.*, ii, 874.
[7] I. Bellucci and G. Savola, *Chem. Zentr.*, 1924, i, 2531; *A.*, ii, 788.

acid) with alizarinsulphonic acid.[8] Distinctive microchemical reactions of zirconium and some other elements with picric acid and with turmeric have also been described.[9]

Picrolonic acid forms characteristic crystals with calcium and can be used as a sensitive microchemical reagent for that metal.[10]

As little as 0·001 mg. of magnesium in 1 c.c. can be detected by the bright blue coloration which it gives with an alcoholic solution of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone.[11]

In view of the lack of sensitiveness of the pyroantimonate test or sodium, it is recommended that a 50% alcoholic solution of magnesium uranyl acetate should be used instead; it is not affected by salts that interfere with the older test.[12]

Several colour reactions have been adapted to the detection of nitric and nitrous acids. A sulphuric acid solution of diphenyldiethylcarbamide gives an intense red coloration with both acids.[13] An aqueous solution of 2 : 4-diamino-6-hydroxypyrimidine or of one of its salts is a sensitive reagent for the zone test for nitrates in presence of sulphuric acid.[14]

Reference may also be made to a method of distinguishing between sulphurous and thiosulphuric acids, based on the pronounced difference in their decolorising action upon aurin, corallin, or rosolic acid.[15]

Quantitative.—By the use of a buffer solution composed of phosphoric, phenylacetic, and boric acids of a total normality of 0·1*N*, it is possible, by adding 0·1*N*-alkali or strong acid, to obtain solutions with a p_H range from 2·5 to 11·5.[16] Tables have also been constructed for determining the p_H values of alcoholic solutions, with the use of several one-colour indicators.[17] A mixture of cresol-red and thymol-blue indicates sharply the half-neutralisation point in carbonate titrations, which can then be completed after the addition of methyl-orange or bromophenol-blue.[18] Of the azo-indicators with asymmetric nuclei, the basic dyestuffs have been shown by means of the spectrophotometer to be the most, and the carboxyl acids the least sensitive.[19] An indicator having approxi-

[8] J. H. de Boer, *Chem. Weekblad*, 1924, **21**, 404; *A.*, ii, 705.
[9] F. Steidler, *Mikrochemie*, 1924, **2**, 131; *A.*, ii, 788.
[10] J. Kisser, *ibid.*, 1923, **1**, 25; *A.*, ii, 124.
[11] F. L. Hahn, H. Wolf, and G. Jäger, *Ber.*, 1924, **57**, [*B*], 1394; *A.*, ii, 784.
[12] I. M. Kolthoff, *Pharm. Weekblad*, 1923, **60**, 1251; *A.*, ii, 60.
[13] L. Desvergnes, *Ann. Chim. anal.*, 1924, [ii], **6**, 102; *A.*, ii, 565.
[14] H. Wolf and E. Heymann, *Z. angew. Chem.*, 1924, **37**, 195; *A.*, ii, 423.
[15] E. Pittarelli, *Arch. Farm. sperim.*, 1924, **38**, 13; *A.*, ii, 777.
[16] E. B. R. Prideaux and A. T. Ward, J., 1924, **125**, 426.
[17] L. Michaelis and M. Mizutani, *Biochem. Z.*, 1924, **147**, 7; *A.*, ii, 623.
[18] S. G. Simpson, *Ind. Eng. Chem.*, 1924, **16**, 709; *A.*, ii, 627.
[19] A. Thiel and F. Wülfken, *Z. anorg. Chem.*, 1924, **136**, 393; *A.*, ii, 622.

mately the same applicability as litmus may be prepared by separating the anthocyanin from an aqueous extract of red cabbage.[20] Prussian blue is another indicator that can be used in titrating an acid with an alkali.[21] In this connexion, attention may be directed to the use of a logarithmic method of constructing titration curves, whereby the degree of neutralisation of a mixture of an acid and a base can be calculated.[22]

Among the indicators recommended for special determinations are diphenylamine for use in the titration of iron with dichromate[23] or permanganate solution,[24] and alkali molybdates [25] and potassium permanganate [26] as indicators for the titration of zinc with ferrocyanide.

The use of various organic dyes (fluorescein, eosin, etc.) as indicators for the titration of silver- and halogen-ion has been recommended,[27] and has been shown to involve a smaller adsorptive error than the use of potassium chromate.[28]

Liquid amalgams have been used as reducing agents in volumetric methods. For example, iron and vanadium may be determined by reducing the ferric iron in one part of the solution with bismuth amalgam, and the vanadium in another portion with zinc amalgam, and titrating both portions with permanganate. Molybdenum and iron may be determined in a similar manner.[29] Liquid zinc amalgam has also been used as the reducing agent for the volumetric determination of phosphoric acid after precipitation as uranyl ammonium phosphate.[30]

Further extensions of the hydrolytic methods of precipitation [31] have been described. For example, titanium may be separated from aluminium by precipitating both metals with ammonia, dissolving the precipitate in sulphuric acid, diluting the solution to a specified p_{H} value, and heating it at 100° to precipitate the titanium.[32] A hydrolytic method has also been adapted to the quantitative separation of bismuth, as a basic nitrate, from lead, copper, and cadmium,[33] and to the determination of barium by

[20] V. Matula, *Chem. Ztg.*, 1924, **48**, 305; *A.*, ii, 496.
[21] K. Jellinek and W. Kühn, *Z. anorg. Chem.*, 1924, **138**, 81; *A.*, ii, 695.
[22] A. Thiel, *ibid.*, 1924, **135**, 1; *A.*, ii, 496.
[23] J. Knop, *J. Amer. Chem. Soc.*, 1924, **46**, 263; *A.*, ii, 351.
[24] T. W. W. Scott, *ibid.*, 1396, *A.*, ii, 787.
[25] K. Fajans and O. Hassel, *Z. Elektrochem.*, 1923, **29**, 450; *A.*, ii, 60.
[26] K. Jellinek and W. Kühn, *Z. anorg. Chem.*, 1924, **138**, 109; *A.*, ii, 695.
[27] K. Fajans and O. Hassel, *Z. anorg. Chem.*, 1924, **137**, 221; *A.*, ii, 776.
[28] W. Böttger and K. O. Schmidt, *ibid.*, 246; *A.*, ii, 776.
[29] K. Someya, *ibid.*, 1924, **138**, 291; *A.*, ii, 787.
[30] S. Saito, *J. Chem. Soc. Japan*, 1924, **45**, 74; *A.*, ii, 780.
[31] Compare *Ann. Report*, 1923, **20**, 169.
[32] L. Kayser, *Z. anorg. Chem.*, 1924, **138**, 43; *A.*, ii, 704.
[33] G. Luff, *Z. anal. Chem.*, 1923, **63**, 330; *A.*, ii, 278.

precipitation as barium pyroborate and hydrolysis of the precipitate to barium hydroxide.[34]

For the separation of the metals of the ammonium sulphide group, the use of hydrogen sulphide under pressure offers many advantages, and conditions for the quantitative precipitation of these metals from their solution in sulphuric acid have been ascertained.[35] Another modification in the use of hydrogen sulphide is its application in a nascent state for the precipitation of platinum and copper, a precipitate free from iron being thus obtained.[36]

When using oxalic acid for standardising permanganate solutions, low results may be obtained owing to adsorption of water by the hydrated acid. This may be avoided by using sublimed anhydrous acid or hydrated acid that has been dried in a current of air previously passed over a mixture of anhydrous and hydrated acid.[37] To prevent the formation of hydrogen peroxide in the titration of oxalic acid with permanganate, it is necessary to work at a temperature of 75° to 85°, and to have a suitable amount of sulphuric or hydrochloric acid present.[38] Pure ferrous ammonium sulphate, however, has been shown to be a more suitable standardising agent than oxalic acid, and it can be used at the ordinary temperature.[3] Metallic silver is also suitable for the standardisation under specified conditions.[40]

A method of determining cuprous oxide in presence of metallic copper and cupric oxide has been based upon its solubility in 3—6 *N*-sulphuric acid, and upon its then reacting with permanganate.[41] Permanganate has also been used for the determination of bismuth after reduction with hydrazine hydrate and solution in an acidified solution of ferric chloride, the ferrous chloride formed being titrated.[42] An analogous method has been devised for determining antimony, the metal being dissolved in warm hydrochloric acid containing a cupric salt, and the amount of cuprous salt titrated with permanganate. In both methods, the solution must be effected in an atmosphere of carbon dioxide.[43]

A method of determining small amounts of molybdenum consists in the reduction of ammonium molybdate or phosphomolybdate

[34] B. N. Angelescu, *Bul. Soc. Chim. România*, 1923, **5**, 72; *A.*, ii, 203.
[35] L. Moser and M. Behr, *Z. anorg. Chem.*, 1924, **134**, 49; *A.*, ii, 503.
[36] R. Doht, *Z. anal. Chem.*, 1924, **64**, 37; *A.*, ii, 569.
[37] W. D. Treadwell and H. Johner, *Helv. Chim. Acta*, 1924, **7**, 528; *A.*, ii, 573.
[38] I. M. Kolthoff, *Z. anal. Chem.*, 1924, **64**, 185; *A.*, ii, 573.
[39] I. M. Kolthoff and J. C. van Dijk, *Pharm. Weekblad*, 1904, **61**, 561; *A.*, ii, 506.
[40] N. A. Tananaev, *Z. anorg. Chem.*, 1924, **136**, 193; *A.*, ii, 628.
[41] D. Nishida and K. Hirabayashi, *J. Chem. Ind. Japan*, 1923, **26**, 1123; *A.*, ii, 125. [42] J. Hanuš and A. Jilek, *Chem. Listy*, 1924, **18**, 8; *A.*, ii, 278.
[43] A. Ecke, *Chem. Ztg.*, 1924, **48**, 537; *A.*, ii, 705.

by means of hydrogen in a silica tube at 700°, solution of the molybdenum in phosphomolybdic acid, and titration of the solution with permanganate.[44]

Potassium permanganate has been shown to be a convenient reagent for standardising thiosulphate solutions for use in iodometric determinations.[45] Among these iodometric methods is one for determining thiosulphate in presence of sulphite, which depends upon the fact that the compound of formaldehyde with sodium hydrogen sulphite is not oxidised by iodine.[46] Another application of iodometry is to the determination of hyposulphite.[47] Magnesium may be determined by precipitation as magnesium ammonium arsenate by means of a standard arsenate solution containing ammonia and ammonium chloride, and iodometric titration of the excess of arsenate in the filtrate.[48]

It has been shown that sodium hypochlorite, which remains stable for a long period, can be used as a substitute for iodine in several determinations, *e.g.*, of tin, antimony, and arsenic[49]; also that bromine can replace iodine, notably in the titration of arsenious acid and of thiosulphate,[50] and of ammonia, sulphurous acid, hydrogen sulphide, and chromates.[51] Nascent bromine produced in a solution of a mixture of bromide and bromate is an excellent oxidising agent for sulphite and thiosulphate, the excess of bromine being afterwards determined iodometrically.[52]

Antimony chloride may be used as a reducing agent in the volumetric determination of hypochlorites and of ferricyanides, the excess of the reagent being titrated with potassium bromate.[53]

Among the new colorimetric methods is one in which bismuth is precipitated as quinine iodobismuthate, the precipitate dissolved in acetone, and the colour compared with a standard,[54] and another in which platinum is determined colorimetrically in the form of its red iodoplatinate.[55] In another method phosphoric acid is determined by precipitation with a nitric acid solution of ammonium

[44] A. Vila, *Compt. rend.*, 1923, **177**, 1219; *A.*, ii, 65.
[45] J. M. Hendel, *Z. anal. Chem.*, 1923, **63**, 321; *A.*, ii, 272.
[46] A. Kurtenacker, *ibid.*, 1924, **64**, 56; *A.*, ii, 564.
[47] Brotherton & Co., Ltd., *Chemistry and Industry*, 1923, **42**, 1131; *A.*, ii, 56.
[48] M. Klingenfuss, *Z. anorg. Chem.*, 1924, **138**, 195; *A.*, ii, 702.
[49] K. Jellinek and W. Krestev, *Z. anorg. Chem.*, 1924, **137**, 333; *A.*, ii, 781.
[50] W. Manchot and F. Oberhauser, 1923, **130**, 161; *A.*, ii, 199.
[51] *Idem*, *Ber.*, 1924, **57**, [*B*], 29; *A.*, ii, 274.
[52] C. Mayr and J. Peyfuss, *Z. anorg. Chem.*, 1923, **127**, 123; *A.*, ii, 56.
[53] F. Feigl and O. Schummer, *Z. anal. Chem.*, 1924, **64**, 249; *A.*, ii, 624.
[54] C. E. Laporte, *J. Pharm. Chim.*, 1923, [vii], 28, 304; *A.*, ii, 68.
[55] E. G. Ardagh, F. S. Seaborne, and N. S. Grant, *Can. Chem. Med.*, 1924, **8**, 117, 140; *A.*, ii, 788.

molybdate and strychnine nitrate, the precipitate dissolved in sodium carbonate solution and heated with phenylhydrazine hydrochloride, and the red coloration compared with a standard.[56] Traces of nitric nitrogen may be determined colorimetrically by means of reduced strychnine and sulphuric acid,[57] but nitrites must be removed or a correction applied for the coloration produced by them before the addition of sulphuric acid.[58]

Many new gravimetric methods for individual metals have been devised. Cadmium may be separated from mercury by precipitation with ammonium thiocyanate and pyridine,[59] and precipitation as copper pyridine thiocyanate has been adapted to the micro-determination of copper.[60] Traces of copper may also be determined as copper benzoinoxime.[61]

For the separation of mercury from arsenic, the precipitated sulphides are treated with cold ammonia, and the undissolved mercuric sulphide is freed from sulphur and dried.[62] Pyrogallol has been used as a reagent for the gravimetric determination of antimony,[63] and the use of cupferron has been extended to the determination of uranium.[64]

In the absence of potassium, rubidium, barium, ammonium salts, and sulphates, perchloric acid may be used for the quantitative precipitation of cæsium.[65] Permutite has been found a suitable reagent for the quantitative separation of ammonia in urine; the final determination is made by the use of Nessler's reagent.[66]

Of the new distillation methods of inorganic analysis, an interesting one is based upon the fact that selenium chloride is volatile in a current of gaseous hydrogen chloride, and may thus be separated from tellurium chloride.[67]

Electrochemistry.

An electrolytic method of removing soluble impurities from completely insoluble precipitates has been based upon the fact that

[56] Y. Terada, *Biochem. Z.*, 1924, **145**, 426; *A.*, ii, 499.

[57] F. M. Scales and A. P. Harrison, *Ind. Eng. Chem.*, 1924, **16**, 571; *A.*, ii, 567.

[58] I. M. Kolthoff, *Chem. Weekblad*, 1924, **21**, 423; *A.*, ii, 779.

[59] G. Rotter, *Z. anal. Chem.*, 1924, **64**, 102; *A.*, ii, 569.

[60] G. Spacu, *Bull. Soc. Stiinte Cluj*, 1922, i, 296; *A.*, 1923, ii, 41.

[61] R. Strebinger, *Mikrochemie*, 1923, **1**, 72; *A.*, ii, 204; compare *Ann. Report*, 1923, **20**, 171.

[62] P. Wenzer and M. Schilt, *Helv. Chim. Acta*, 1924, **7**, 907; *A.*, ii, 873.

[63] F. Feigl, *Z. anal. Chem.*, 1924, **64**, 41; *A.*, ii, 571.

[64] J. A. Holliday and T. R. Cunningham, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 329; *A.*, ii, 125.

[65] E. Murmann, *Oesterr. Chem. Ztg.*, 1923, **26**, 164; *A.*, ii, 60.

[66] A. Kolb, *Chem. Ztg.*, 1924, **48**, 557; *A.*, ii, 699.

[67] V. Lenher and D. P. Smith, *Ind. Eng. Chem.*, 1924, **16**, 837; *A.*, ii, 698.

adsorbed substances, when subjected to the action of an electric current, are completely dissolved and pass towards the electrode of the opposite sign to that they bear. By this means aluminium hydroxide can be freed from entangled impurities, and ferric oxide from chromic acid.[68]

Advantages have been claimed for the use of various kinds of electrodes, such as a rigid mercury cathode as a substitute for one of platinum gauze for the deposition of various metals, including zinc, bismuth, lead, cobalt, iron, and nickel, under specified conditions [69]; also for the use of glass electrodes for the determination of hydrogen-ion concentration.[70] The quinhydrone electrode has been shown to give trustworthy results in determining the hydrogen-ion concentration of solutions more acid than $p_H 8$, in the presence of a buffer, provided that substances with strong reducing or oxidising action are not present.[71] Mention may also be made of some simple forms of hydrogen electrode, one of which has been adapted to micro-determinations.[72]

The special applications of electrolytic processes include a rapid method of separating silver, copper, and bismuth by the use of graduated potentials,[73] and a micro-method for separating gold from potassium cyanide solution.[74]

An electrometric method of titrating silver ions in the presence of colloidal silver [75] has been devised. To obtain accurate results in the electrometric titration of mercury with ammonium thiocyanate, it is essential that mercury ions should not be present; the uncertain end-point in titrating mercuric nitrate is due to hydrolysis, and to prevent this a large excess of acid should be added.[76]

It has been found that, of the different ferrocyanides, only the potassium salt gives good results in the electrometric titration of zinc. In the presence of cæsium, a double ferrocyanide of zinc and cæsium is formed, and the end-point is not sharp, but rubidium, contrary to what has been stated,[77] has no effect on the composition of the precipitate.[78]

[68] A. Charrion, *Compt. rend.*, 1924, **178**, 934; *A.*, ii, 345.

[69] H. Paweck and E. Walther, *Z. anal. Chem.*, 1924, **64**, 89; *A.*, ii, 562.

[70] A. L. von Steiger, *Z. Elektrochem.*, 1924, **30**, 259; *A.*, ii, 696; W. E. Brown, *J. Sci. Instruments*, 1924, **2**, 12; *A.*, ii, 869.

[71] V. K. LaMer and T. R. Parsons, *J. Biol. Chem.*, 1923, **57**, 613; *A.*, ii, 55.

[72] F. J. Considine, *Analyst*, 1924, **49**, 332; *A.*, ii, 562.

[73] A. Lassieur, *Compt. rend.*, 1924, **178**, 847; *A.*, ii, 568.

[74] K. Fuchs, *Mikrochemie*, 1923, **1**, 86; *A.*, ii, 207.

[75] K. von Neergaard, *Arch. Expt. Path. Pharm.*, 1923, **100**, 162; *A.*, ii, 124.

[76] R. Müller and O. Benda, *Z. anorg. Chem.*, 1924, **134**, 102; *A.*, ii, 502.

[77] W. D. Treadwell and D. Chervet, *Helv. Chim. Acta*, 1922, **5**, 633; *A.*, 1922, ii, 786.

[78] I. M. Kolthoff and E. J. A. H. Verzijl, *Rec. trav. chim.*, 1924, **43**, 389; *A.*, ii, 501.

An electrometric method of determining barium, even in the presence of calcium, has been based upon the fact that, on shaking freshly precipitated lead sulphate for 24 hours with barium chloride solution, about 98% of the barium is converted into barium sulphate, the amount of which is determined by titrating the lead in solution electrometrically with potassium ferrocyanide.[79] An analogous method of determining soluble sulphates consists in adding alcohol to the solution, then a measured excess of standard lead nitrate solution, and titrating the excess of lead in the filtrate from the precipitated lead sulphate.[80]

A method of titrating chlorides with a mercurous solution has been devised, in which the end-point is determined electrometrically with an amalgamated platinum electrode; it has also been shown that nitrates may be determined by means of their oxidising action on ferrous sulphate and electrometric titration of the ferric salt with titanous chloride solution.[81]

Fairly accurate results can be obtained in the titration of chromic acid with alkali, either with the use of a hydrogen electrode, or with the usual oxygen electrode, the electrometric end-point occurring somewhat later than the end-point as indicated by phenolphthalein.[82]

An electrometric method of determining carbon dioxide (accurate to 0·002%) has been devised for the study of photosynthesis, the air being passed through a solution of barium hydroxide, the conductivity of which is then determined.[83]

For the electrometric determination of formaldehyde, advantage has been taken of the fact that silver nitrate is quantitatively reduced to metallic silver by formaldehyde in presence of an excess of sodium carbonate. After the reduction, the excess of silver (present as carbonate) is determined electrometrically by titration with potassium chloride (after neutralisation), or with potassium iodide (without neutralisation).[84]

Water Analysis.

A method of determining dissolved air in small quantities of water has been based upon the fact that when potassium hydroxide or certain salts, such as ammonium chloride or sulphate, are dissolved in the water, the air is expelled and can be collected and measured

[79] E. Müller and R. Wertheim, *Z. anorg. Chem.*, 1924, **135**, 269; *A.*, ii, 568.
[80] *Idem*, *ibid.*, 1924 **133**. 411; *A.*, ii, 564.
[81] E. Müller, *Z. Elektrochem.*, 1924, **30**, 420; *A.*, ii, 777.
[82] H. T. S. Britton, J., 1924, **125**, 1572.
[83] H. A. Spoehr and J. M. McGee, *Ind. Eng. Chem.*, 1924, **16**, 128; *A.*, ii, 275.
[84] E. Müller and W. Low, *Z. anal. Chem.*, 1924, **64**, 297; *A.*, ii, 706.

in a small graduated apparatus filled with mercury. Subsequently, the oxygen is absorbed by means of alkaline pyrogallol and the nitrogen measured.[85]

It has been shown that precipitation of the total carbon dioxide in hard waters by means of calcium hydroxide or barium hydroxide and titration of the excess of precipitant give low results, but that by adding a small amount of calcium carbonate to a solution of calcium hydroxide and calcium chloride a reagent that gives quantitative results in this method is obtained.[86]

In determining minute quantities of lead and copper together in water by Winkler's colorimetric method, the results for copper (obtained from the difference between the colorimetric reading for the two metals together and that for lead alone, after solution of the colloidal copper by the addition of cyanide) require correction, since the colour of lead sulphide is less intense than that of copper sulphide.[87] The presence of copper also interferes with the sensitiveness of Thresh's colorimetric method of determining lead by means of a gelatin and acid solution and of hydrogen sulphide.[88] A better method of preparing the reagent has been devised, and the process has been shown to give accurate results for determining traces of lead both in water and in urine.[89]

A new method of determining small quantities of calcium and magnesium depends upon their forming micro-crystalline precipitates of the respective ferrocyanides. The reagent consists of a solution of ammonium ferrocyanide containing 50% of alcohol, and it may be used for determining the amounts of calcium and magnesium separately, or the hardness of a water, by measuring with a nephelometer the white turbidity that it produces.[90]

A colorimetric method of determining soluble aluminium in water with an accuracy of 0·01% has been based upon the well-known colour reaction of aluminium with hæmatoxylin. The p_H value is first brought to 8·2—8·3 by the addition of ammonium carbonate, and acetic acid is added before comparison with the standard solution, to eliminate the influence of iron and magnesium salts.[91]

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[85] H. S. Becker and W. E. Abbott, *J. Soc. Chem. Ind.*, 1923, **42**, 484T; *A.*, ii, 200.
[86] E. M. Crowther and W. S. Martin, J., 1924, **125**, 1937.
[87] C. Pyriki, *Z. anal. Chem.*, 1924, **64**, 325; *A.*, ii, 702.
[88] J. C. Thresh, *Analyst*, 1921, **46**, 270; *A.*, 1921, ii, 551.
[89] *Idem*, *ibid.*, 1924, **49**, 124; *A.*, ii, 124.
[90] F. Feigl and F. Pavelea, *Mikrochemie*, 1924, **2**, 85; *A.*, ii, 784.
[91] W. D. Hatfield, *Ind. Eng. Chem.*, 1924, **16**, 233; *A.*, ii, 350.

BIOCHEMISTRY.

For some time past it has been evident that, with the rapid advance in the knowledge of the chemical processes of the living cell, it was becoming increasingly difficult to discuss many of them adequately in separate sections devoted to plant and animal chemistry. The conviction that to continue to do so would inevitably tend to narrow the outlook has led, this year, to a fusion of the Annual Report on Physiological Chemistry with that on Agricultural Chemistry and Vegetable Physiology. By this means it is hoped to present, in one annual Report on Biochemistry, that broader conception of many fundamental biological changes, as, for example, the degradation of dextrose, whether effected by muscle cells, by yeast, or by the cells of the higher plants, which is essential to the progress of this great branch of Chemistry.

It must be pointed out that this fusion of the two Reports involves the inclusion, under the general title of Biochemistry, of the chemistry of the soil, a branch of agricultural chemistry that has always figured in the past as part of the Report on Agricultural Chemistry and Vegetable Physiology. This of course is as it should be, since the logical sequence is to consider first the medium in which the plant grows, then the plant itself, and then finally the animal that feeds on the plant.

In the case of the present Report, the opening section, that on Soils, is devoted mainly to a discussion of the inorganic and physical chemistry of the soil. No apology is made for this, since the proper understanding of the factors controlling the biological processes in the soil and the uptake of essential elements by the plant necessitates a consideration of the soil in all its aspects; attention is directed to the fact merely to explain the apparent anomaly of a report on biochemistry the first part of which is seemingly wholly unconnected with the chemistry of biological processes.

It must also be mentioned that consideration of the chemistry of enzyme action and fermentation has been again deferred to another year, as it was not felt that these subjects have advanced sufficiently since they were last reviewed to justify giving up to them space that could be better employed on other branches of biochemistry more in need of discussion.

In the last two Reports, published work on all the main aspects

of soil and plant chemistry was used in an attempt to give an account of the relations of these different aspects to one another, and so to sketch in the main lines of the subject as a whole. In this Report, certain aspects of the subject have been selected for fuller and more detailed discussion, and others have been entirely omitted, these being left over for similar special treatment in subsequent Reports.

Soils.

The Nature and Properties of Soil Constituents.

The two chief constituents of a soil that characterise it and serve to distinguish it from a mass of unweathered rock fragments are (*a*) the dark-coloured humic matter, and (*b*) the complex inorganic material which forms the chief constituent of clay.

The Humic Matter of the Soil.—In recent Reports attention has been directed to the uncertainty that exists as to the origin and mode of formation of the humic matter in the soil.[1] One group of workers regards this material as a product of decomposition of cellulose or other carbohydrates, whilst other investigators hold the view that it is derived from aromatic substances of a phenolic nature, among which lignin is included. Various considerations render the latter alternative the more attractive one, and during the past year further evidence has been advanced which considerably strengthens this view.

F. Fischer,[2] who advanced the hypothesis that lignin is the parent substance of humic acid in 1921, has cited the work of Bray and Andrews[3] in support of that view. These authors showed that during the bacterial decay of wood the cellulose had almost disappeared in the space of three years, whereas the lignin had suffered little diminution in amount. Schwalbe's[4] experiments, in which he prepared a substance resembling coal by the action of powerful dehydrating agents on cellulose, are held not to be valid in determining the origin of coal, because the conditions were so different from those prevailing in nature. It is far more probable that dead vegetation would be rapidly subject to bacterial decay, with consequent destruction of cellulose, and that humic matter (and subsequently coal) would be produced by chemical autoxidation of the lignin, which is much more resistant to bacterial action.

H. Tropsch and A. Schellenberg carried out in 1921 a series of investigations on the products of dry distillation of humic acid

[1] *Ann. Reports*, 1922, **19**, 204; 1923, **20**, 209.

[2] *Brennstoff-Chem.*, 1924, **5**, 132; *A.*, i, 715.

[3] *J. Ind. Eng. Chem.*, 1924, **16**, 137.

[4] C. G. Schwalbe and R. Schepp, *Ber.*, 1924, **57**, [*B*], 319, 881; *A.*, i, 377, 715

(prepared from coal) and of its interaction with various reagents such as potassium hydroxide, nitric acid, sulphuric acid, chlorine. The results of this work have only recently become generally available.[5] They show that relatively simple aromatic substances are readily formed from humic acid, and that humic acid and lignin behave similarly. Cellulose and dextrose, and artificial humic acid prepared from sugar, however, behave somewhat differently. F. Fischer and H. Tropsch [6] have extended this work by a comparison of the behaviour of cellulose and of lignin on hydrogenation with hydriodic acid under pressure, and on treatment with caustic alkalis. The results of this work also support the view that lignin rather than cellulose is the parent substance of humic acid, whilst the work of A. R. Pearson [7] on the oxidation of humic matter from coal with bromine and alkali also points in the same direction. As pointed out by H. Tropsch,[8] the occasional occurrence of small quantities of cellulosic material in coal is no proof that coal (and humic acid) is produced from cellulose. On the theory that cellulose is converted into coal by the action of heat and pressure it is far more difficult to account for the survival of cellulose here and there than it is on the supposition that cellulose disappears by the action of micro-organisms, in which case the local occurrence of aseptic conditions would readily explain this survival.

Recent work in the reporter's laboratory at Rothamsted has provided evidence for the lignin hypothesis of the origin of humic matter, from quite a different direction. From a study of the fractionation of organic matter in mineral soils, C. W. B. Arnold [9] obtained results indicating that the humic matter in Rothamsted soils manured and cropped in various ways was of the same character in all cases; this fact can most readily be explained on the hypothesis that humic matter is formed in the soil from one common constituent of all plant residues, and that its amount depends on the amount of this common constituent in the organic matter supplied to the soil, all the other organic constituents so supplied being completely destroyed by biological agencies. The natural inference to draw, in view of the facts discussed above, is that this humus-forming constituent is lignin. Following up this idea, M. S. du Toit [10] has studied the relation between the amount of humic matter formed when various plant materials are allowed to rot down in the presence of soil organisms and the amounts of

[5] *Ges. Abh. Kenntn. Kohle*, 1921, **6**, 191, 196, 214, 235, 248, 257; *A.*, i, 619—621.

[6] *Ber.*, 1923, **56**, [*B*], 2418; *A.*, i, 148.

[7] *Fuel*, 1924, **3**, 297; *A.*, i, 620.

[8] *Brennstoff-Chem.*, 1924, **5**, 288.

[9] Not yet published.

[10] M. S. du Toit, "The Origin and Mode of Formation of the Humic Matter of the Soil." Ph.D. Thesis, Cambridge, 1924.

the chief constituents (cellulose, pentosans, lignin) that have been destroyed. There was no correlation between humic matter produced and either cellulose or pentosans destroyed, but in all cases the disappearance of lignin was paralleled by the production of humic matter. Moreover, when pure carbohydrates (cellulose, pentosans, sugars) were decomposed by soil organisms, their complete disappearance was not attended with the production of any humic matter whatever.

There is thus on the whole quite a large body of evidence in favour of the hypothesis that the humic matter of the soil is derived from lignin and not from carbohydrates. A definite proof of the validity of this hypothesis must provide evidence of the identity of the natural product with the humic acid produced artificially from lignin, and before such identity can be established, improvements in the methods of purifying the natural product are needed.

That the so-called humic acid of the soil is indeed a true acid was clearly shown by Odén [11] for the product obtained from peat. The application of similar methods (conductometric titration) to purified humic acid from Rothamsted soil and to the artificial product obtained by the oxidation of lignin showed that both of these substances behave in the same way as Odén's peat humic acid,[10] and therefore must be regarded as true acids of high molecular weight, practically insoluble in the free state, but readily giving colloidal solutions. Their salts with alkali metals are soluble and behave as colloidal electrolytes, whilst their salts with other metals are insoluble.

The Inorganic Colloidal Material of the Soil.—Many interesting problems arise from the consideration of the chemical processes that occur in the formation of soil and the weathering of minerals, and increasing attention is being directed to this subject on the Continent, following the lead of Glinka and the Russian School, and in the United States. A detailed discussion of this part of the subject must be deferred to another year, but reference may here be made to a useful summary which has been published by G. W. Robinson.[12]

In temperate regions, the product of this weathering is a colloidal material, the characteristic constituent of clay, containing silica, aluminium and ferric oxides together with a certain amount of bases. The older the soil is, the greater is the loss of these bases by leaching, and under certain conditions they may be entirely removed. According to the degree of depletion of bases, the residual colloid exhibits a greater or less degree of acidity. The cause of the acidity has been the subject of much controversy, but during the

[11] *Trans. Faraday Soc.*, 1922, **7**, 288. [12] *Geol. Mag.*, 1924, **61**, 444.

past two or three years a number of important investigations have been carried out as a result of which the position of the whole subject has been considerably clarified.

Reference was made in last year's Report [13] to the work of Bradfield, in which, from an examination of the colloidal material separated from a subsoil clay by the use of the "super-centrifuge," he showed that this colloidal material could not be regarded as being made up of a *mixture* of the hydrates of silica, alumina, and ferric oxide, but that it consisted of a definite compound or mixture of compounds in which the three constituent oxides were chemically combined in the form of complex aluminosilicates. W. O. Robinson and R. S. Holmes [14] have since published the results of an investigation into the chemical composition of the soil colloids from forty-five soils from the United States. The colloidal matter was separated by the "super-centrifuge" and analysed. It was found that only a small part of this material consisted of finely divided, unweathered mineral fragments, and that most of it consisted of material that behaved as an intimate mixture of complex aluminosilicates, not as a mixture of the separate constituent oxides, thus confirming the results of Bradfield. There were apparently two forms of iron present, one a hydrous ferric oxide, presumably in the free state, and the other some compound without red or yellow colour, presumably a silicate.

During the past year Bradfield has published two important papers which must be considered in some detail. In one of his earlier papers [15] he showed that sharp end-points could be obtained in conductivity titrations of clays or soils if these were carried out in such a manner as to make possible the detection of the end-point in the neutralisation of a weak acid by a strong base, that is, by the gradual addition of the clay suspension to a fixed quantity of the strong base, instead of in the reverse manner as had been done in most previous investigations. The titration curves then bore no resemblance to an "adsorption isotherm," but indicated that definite weak acids were being neutralised. This was supported by the further result that practically equivalent amounts of different bases were needed for the attainment of neutralisation as indicated by the breaks in the titration curves. He advanced cogent arguments to show that the results used by Salter and Morgan [16] in favour of the view that the reaction between clay and alkalis is a physical adsorption are really less compatible with that

[13] *Ann. Reports*, 1923, **20**, 201.
[14] U.S. Dept. of Agric., Dept. Bulletin No. 1311, 1924, pp. 1—41.
[15] *Ann. Reports*, 1923, **20**, 204.
[16] *J. Physical Chem.*, 1923, **27**, 117; *A.*, 1923, i, 523.

view than with what would be expected from the chemical interaction of bases with a colloidal, high-molecular, weak acid. Bradfield has now produced further evidence in favour of the latter view.[17] He prepared a series of suspensions of the same colloidal clay material, containing varying proportions of water, and determined the hydrogen-ion concentration of these by the hydrogen electrode method. The curve obtained by plotting hydrogen-ion concentration against dilution was compared with that showing the hydrogen-ion concentration of solutions of acetic acid at varying dilutions. The two curves were very similar in form, from which it appears that the colloidal matter behaves as a true acid, although probably much weaker than acetic acid. In another paper [18] Bradfield has described the result of further experiments in which he has studied the influence of the hydrogen-ion concentration on the flocculation of clay suspensions by electrolytes and on absorption and base exchange. Although the total amounts of acids of different strengths needed to flocculate colloidal clay suspensions may vary widely if expressed in terms of the titratable acidity, flocculation occurred at about the same hydrogen-ion concentration in all these cases. Further, when a suspension of an acid colloidal clay was flocculated with solutions of p_H varying between 3 and 11, but all containing the same concentration of potassium, the electrolyte requirement increased gradually as the hydrogen-ion concentration decreased, until the neutral point was approached; then the amount of electrolyte required increased rapidly until a p_H of 8·5 was reached, and remained constant from there to p_H 12. This sudden increase at the neutral point in the case of an acid clay is taken to indicate that the alkaline mixtures have an additional function compared with the other mixtures: they must neutralise the clay acids, then flocculate the resulting potassium salt. This conclusion is supported by the fact that a neutral clay showed no marked change in electrolyte requirement at the neutral point. Moreover, when varying concentrations of acid clay are used, the amount of potassium required for flocculation in the alkaline region increases in proportion to the increase in concentration of the clay. Besides the significance of these results in their bearing on the nature of the acidity of acid soils and on the chemical nature of the colloidal clay substance, they are also of importance as indicating that in studies on the flocculation of clay suspensions comparable results cannot be obtained unless due attention is paid to the hydrogen-ion concentration, and the concentration of the suspension, as well as to the reaction of the clay under investigation.

The absorption of kations from neutral salts by clays, and the

[17] *J. Physical Chem.*, 1924, **28**, 170. [18] *Soil Sci.*, 1924, **17**, 411; *A.*, i, 927.

exchange of bases, are also influenced by the hydrogen-ion concentration. Determinations of the amounts of total bases in the solution obtained when a series of solutions of varying p_H but of constant potassium content were added to a suspension of an acid colloidal clay showed that the sign and magnitude of the " base balance " depended on the p_H of the solution : when the hydrogen-ion concentration of the solution was greater than that of the clay suspension, the amount of potassium absorbed (*i.e.*, removed from the solution) was less than the amount of other bases liberated (expressed in equivalents)—there was a positive " base balance," which was greater the greater the excess of the hydrogen-ion concentration of the solution above that of the clay suspension. When, however, the solution had a lower hydrogen-ion concentration than the clay suspension, the number of equivalents of potassium absorbed was greater than that of the other bases liberated—the base balance was negative, the magnitude of this increasing steadily up to a p_H of about 11 and then changing more slowly. Only when the reaction of the solution was the same as that of the clay suspension was there a chemically equivalent base exchange in which the amount of other bases appearing in the solution was equivalent to the amount of potash absorbed.

If the clay material be regarded as a true acid, the interpretation of these results is comparatively simple. An acid colloidal clay which still contains replaceable bases must be regarded as a complex acid salt. If this acid salt is treated with a more acid solution, the net result will be the liberation of some of the bases from the acid salt with the production of a still more acid salt; if, on the other hand, the solution added to the acid salt is itself less acid (*i.e.*, more alkaline), the net result will be the neutralisation of a part of the residual acidity of the acid salt—the production of a clay in which a greater proportion of the acidic hydrogens have been replaced by basic kations.

These results serve not only to clear up many anomalies and contradictions in past work on " adsorption " and base exchange, in which no attention was paid to the hydrogen-ion concentration of the medium, but they also provide a satisfactory basis for the interpretation of the phenomena of soil acidity, " adsorption " and base exchange on purely chemical lines.

The demonstration of the acidic character of the clay substance, and of its behaviour in a manner consistent with that acid character over a wide range of p_H, raises the question of whether there is any real foundation for the view put forward a few years ago by S. Arrhenius,[19] according to which, clay may act as an ampholyte

[19] *J. Amer. Chem. Soc.*, 1922, **44**, 521; *A.*, i, 707.

and display a behaviour analogous to that of proteins, in accordance with the explanation of Loeb. Bradfield [20] has shown in an earlier paper that the flocculation experiments on which Arrhenius based his view are susceptible of another interpretation, in which the Donnan effect may be concerned.[21] His cataphoresis experiments afforded no support for Arrhenius's view, nor does the behaviour of clay throughout the range of hydrogen-ion concentration used in the experiments described above give any indication of the possession of amphoteric properties by the clay. W. C. Dayhuff and D. R. Hoagland [22] have now made a careful series of cataphoresis measurements with an acid clay over a range of hydrogen-ion concentrations between p_H 2·1 to 12·7. Their results indicated that throughout the whole of this range the clay particles carried a negative charge: they always moved towards the kathode. The above range of p_H more than covers that in which all soils fall, so that it may be taken as established that under natural conditions clay does not behave as an ampholyte. It is, of course, possible that outside the above range of p_H clay might exhibit amphoteric properties, but it must be borne in mind that under the strongly alkaline or acid conditions obtaining outside that range secondary chemical reactions are likely to be involved in which decomposition of the complex aluminosilicic acids of the clay would occur, with the production of silica, which carries a negative charge, and of alumina and ferric oxide, which carry positive charges.

Many workers have advanced interpretations of the behaviour of clay suspensions to flocculating agents, in which absorption of hydroxyl ions was assumed in order to explain the stabilising influence of alkali in certain concentrations. Dayhuff and Hoagland, in discussing their results, point out how such an assumption is unnecessary, and they indicate how, according to the results of Bradfield, Mattson,[23] and other workers, the predominant factors determining the stability of clay suspensions may be the nature and concentration of the kation present in the medium.

The Chemical Interpretation of the Phenomena of "Adsorption" and Acidity in Soils.

In last year's Report [24] special attention was directed to the question of alkali soils, and after reference to the pioneering work of Gedroiz in this field, and to the important investigations of

[20] Missouri Agri. Expt. Sta. Res. Bull. 60, 1923.

[21] The application of the Donnan effect to soils is also discussed by N. M. Comber, *Trans. Faraday Soc.*, 1924.

[22] *Soil Sci.*, 1924, **18**, 401.

[23] S. E. Mattson, *Koll. Chem. Beihefte*, 1922, **14**, 227; *A.*, 1922, i, 800.

[24] *Ann. Reports*, 1923, **20**, 205.

Hissink, the work of Cummins and Kelley on the formation of "black alkali" soils was discussed in some detail. This aspect of base exchange in soils may therefore be passed over in this Report, and the remainder of this part of the Soils section will be devoted to a brief discussion of the existing state of our knowledge of the facts of base exchange in soils with special reference to their bearing, in the light of the above discussion, on the mechanism of absorption by soils and on soil acidity.

When a neutral soil is treated with a solution of a neutral salt, an exchange of kations takes place, the cardinal features of which are: (i) The amount of the kations of the neutral salt that are removed from the solution is stoicheiometrically equivalent to the amount of the other kations that are given up to the liquid by the soil. The anion of the neutral salt is not changed in concentration. Salts of acids, such as phosphoric, that give insoluble precipitates with calcium, aluminium, and other soil constituents, are of course excluded from these considerations.[25]

(ii) This exchange of kations occurs practically instantaneously.

(iii) The extent to which this exchange takes place varies exponentially with the equilibrium concentration of the entering kation (*i.e.*, that of the neutral salt used), thus conforming to the general type of Freundlich's adsorption curves and equations.

By continually leaching a soil with fresh portions of a neutral salt solution, the equilibrium is continually disturbed, and the soil can thus be brought into such a condition that the whole of its absorbed kations are of one kind. The physical and other properties of the resulting soil vary markedly with the nature of the absorbed kation, as is well illustrated in connexion with alkali soils.

The absorbing material of soils that are acid (that is, soils the aqueous suspensions of which have p_H values of less than 7·07), contains a smaller amount of exchangeable bases than that of neutral soils; these acid soils are "unsaturated," and in general the greater their degree of unsaturation the more acid they are.

Base exchange in neutral soils does not present any special features that need cause controversy between the upholders of the physical theory of absorption and those who prefer to regard the phenomena as essentially chemical. When, however, acid—"unsaturated"—soils are considered, especially with reference to the behaviour of such soils on treatment with neutral salts and with alkalis, we are on much more contentious ground. Such soils, on treatment with a neutral salt, give an acid reaction to the liquid, the acidity so developed being known as "latent" or "exchange" acidity. This acidity is due to a hydrogen-ion concentration that is

[25] N. M. Comber, *loc. cit.*

higher than that of the "actual" or "active" acidity of the soil, which is the acidity shown by the soil suspension in water. Finally, there is another form of acidity, the "total" acidity, which represents the amount of base that must be added to bring the soil to neutrality. The upholders of the hypothesis of physical "adsorption" in soils explain the "exchange" acidity as due to the selective adsorption of the kation of the neutral salt, leaving the anion in the solution, while the "total" acidity is due to the fact that the soil can absorb basic hydroxide as a whole.

Only recently has it been pointed out, by Gedroiz [26] in Russia and by Hissink [27] in Holland, that all these phenomena can be brought into line if we look upon the absorbing material of the soil as having a definite saturation capacity for kations, and further, if we assume that the absorbing material can absorb hydrogen ions as well as metallic kations. The absorbing material of a soil is then always saturated with a constant amount of kations, the only difference being that in an acid soil a larger proportion of these kations are hydrogen ions than is the case with a neutral soil. Such an acid soil gives rise to a definite hydrogen-ion concentration in aqueous suspension, this being the equilibrium concentration for the liquid phase in equilibrium with the absorbed ions of the solid phase. When the soil is treated with a salt solution, there is an exchange between the kations of the neutral salt and hydrogen ions absorbed by the solid phase, so that at equilibrium the latter contains a greater proportion of absorbed basic kations and the liquid phase contains a greater concentration of hydrogen ions. The extent to which this exchange takes place depends on the strength of the acid the salt of which is used. In the case of the salt of a strong acid such as hydrochloric acid, the amount of titratable acidity liberated is small, but in the case of the salt of a weak acid such as acetic acid, the titratible acidity developed is much larger, since, owing to the low dissociation of acetic acid, a much greater displacement of hydrogen ions from the solid phase can occur before the equilibrium concentration of hydrogen ions in the liquid phase is reached. Further, the addition of an alkaline hydroxide to an acid salt can similarly be pictured as an exchange of basic kations for hydrogen ions, only in this case the liberated hydrogen ions

[26] K. K. Gedroiz, "On the Absorptive Power of Soils." Editorial Committee of the People's Commissariat of Agriculture, Leningrad, 1922; *Zhur. Opit. Agron.*, 1924, **22**, 3. A complete set of translations of Gedroiz's papers on the subject of absorption and base exchange is in the possession of the reporter (H. J. P.), through the courtesy of the U.S. Dept. of Agriculture. Workers in this field who are desirous of studying these translations should communicate with H. J. P. at Rothamsted.

[27] *Trans. Faraday Soc.*, 1924.

combine with the hydroxyl ions in the solution to form water, and hence the absorption of the base goes on without the appearance of other kations in the liquid.

The soluble iron and aluminium that are found in acid soils, and that appear to a marked extent in the acid solution obtained by treating these soils with neutral salt solutions, can most readily be regarded as being liberated by secondary reactions between the acid liberated and some constituents of the solid phase, although it is not impossible that they may exist, at least in part, as exchangeable kations absorbed by the solid phase, and liberated by exchange in the same way as other kations.

From the above discussion it will be seen that it is possible to explain the phenomena of absorption by soils, soil acidity, and base exchange as all due to the occurrence of ionic exchanges, which occur owing to the absorptive material of the soil having a definite affinity for kations, including hydrogen ions. By itself, however, this explanation does not carry matters very much further, for although it brings a number of apparently differing phenomena into one category, it still leaves unanswered the question of the nature of the attraction whereby the absorbing material of the soil absorbs kations. Here, however, the results of Bradfield that are discussed on pp. 175–178 are of importance. Hissink [27] explains the absorptive capacity of the soil as due to the existence of colloidal acids, which are ionised at the interface between the solid and the liquid phase, so that an electrical double layer is formed at that interface, with the negatively charged complex colloidal anion on the solid phase side of the double layer and with positively charged hydrogen or metallic ions on the liquid side. Now that Bradfield has clearly demonstrated that the colloidal clay material of soils does actually behave as a true acid, this fact, together with the proof that the humic acids of soils are also true acids, provides a sound experimental basis for Hissink's hypothesis, and it is possible to explain all the phenomena in question as chemical ionic reactions of weak acids (clay acids and humic acids), these reactions being localised at a solid–liquid interface owing to the fact that these acids are insoluble and present in the soil as colloidal particles or as a gel on the surface of mineral soil particles. The practically instantaneous nature of the reaction is, of course, what would be expected of ionic interchanges of this nature; moreover, the localisation of the ionic exchanges at a surface necessarily places the equilibrium conditions in a different category from those obtaining for reactions which take place wholly in the liquid phase. The exponential character of the relation connecting the equilibrium concentration of the entering ion in the liquid phase with the amount

of it which has been absorbed is what would be expected in a system of this sort. As has been pointed out by E. A. Fisher [28] and others, the fact that a given set of data can be represented by an exponential curve, and made to fit a Freundlich "adsorption" equation, is no evidence that the reaction in question is a physical adsorption. Many purely chemical reactions in a heterogeneous system conform to an equation of the same type.

In the short space of this discussion it is not possible to follow the application of this hypothesis to the detailed phenomena of the soil, nor for that matter must it be regarded as more than a tentative one at present, as much experimental work still remains to be done. It does, however, appear that this hypothesis renders unnecessary the assumption of the existence of purely physical "adsorptions" in the soil. In following the detailed application of these views it is necessary to take account of the relative intensity with which different ions are held by the absorbing material, and the influence of the degree of hydration of the ions. Gedroiz [29] has recently made a very interesting and convincing study of the physical properties of the soil from this point of view, but considerations of space do not allow of the discussion of this work here.

The views developed in the above discussion depend on or are relevant to a number of recent papers in addition to those actually cited. Detailed reference to these was omitted above in order to allow of a broad presentation of the main outline of the subject. Some of the more important of these other papers are noted below.[30]

The Influence of Soil Acidity on Plant Growth.

The effect of soil acidity on plant growth may depend on factors other than the actual hydrogen-ion concentration of the soil, such as, for instance, the presence of soluble aluminium compounds.[31] There is a tendency in several recent papers to direct attention to the fact that on many acid soils the factor deleterious to crop growth

[28] E. A. Fisher, *Trans. Faraday Soc.*, 1922, **17**, 305.

[29] K. K. Gedroiz, *Zhur. Opit. Agron.*, 1924, **22**, 29.

[30] W. P. Kelley and S. M. Brown, Univ. Calif. Pub. Agric. Sci. Techn. Paper No. 15, 1924, pp. 1—39. J. W. Tidmore and F. W. Parker, *Soil Sci.*, 1924, **18**, 331; *A.*, i, 1394. H. J. Page and W. Williams, *Trans. Faraday Soc.*, 1924. H. Kappen, *Z. Pflanz. Düng.*, 1924, [*A*], **3**, 209; A. Densch, *ibid.*, 218; E. Ramann, *ibid.*, 257. W. Hummelschen and H. Kappen, *ibid.*, 289. O. Lemmermann and L. Fresenius, *ibid.*, p. 1; [*B*], **3**, 233.

[31] *Ann. Reports*, 1922, **19**, 213; 1923, **20**, 207. See also Whiting, *J. Amer. Soc. Agron.*, 1923, **15**, 277; *A.*, i, 928. W. T. McGeorge, *Soil Sci.*, 1924, **18**, 1. S. D. Conner, *J. Ind. Eng. Chem.*, 1924, **16**, 173. G. N. Hoffer and J. F. Trost, *J. Amer. Soc. Agron.*, 1923, **15**, 323; *A.*, i, 925.

may not be acidity, but lack of sufficient calcium.[32] This is well illustrated by the papers by G. W. Robinson, C. O. Swanson, P. L. Gainey and W. L. Latshaw, and Duley.

Seldom, if ever, is a cultivated soil so acid that it does not still contain a certain amount of replaceable kations, mainly consisting of calcium, but when this amount falls below a certain value, crop failure owing to calcium starvation is liable to occur. If, on the other hand, the amount of replaceable, or readily soluble, calcium is above this value, the soil may still be quite acid, and yet many crops will flourish on it. The " lime requirement " of a soil, which is not a soil " constant " but necessarily varies according to the type of crop and to other conditions, is thus usually, in practice, definitely less than the amount of lime needed to bring the soil to neutrality (p_{H} 7·07). It is important to remember that even at neutrality the soil colloids are still far from saturated; they still contain replaceable hydrogen ions, as evidenced by the fact that by the addition of a neutral salt to a faintly alkaline soil the reaction of the solution is usually brought slightly on to the acid side. This would, of course, be expected in the case of a weak acid, which would exist wholly as a salt (*i.e.*, free from replaceable hydrogen ions) only at a p_{H} well on the alkaline side. Thus the actual percentage saturation with calcium of a soil that is definitely acid may be relatively only slightly less than that of the soil at neutrality, and it may often be necessary for the hydrogen-ion concentration of the soil to become very marked before the degree of saturation of the absorbing material with calcium is so much lowered that there is insufficient readily available calcium to meet the needs of the plant.

Biochemical Changes in the Soil.

This branch of the subject has been rather fully discussed in the Reports for 1922 and 1923,[33] so that in order to leave space in this Report for the fuller treatment given to other branches of the subject, consideration of the work published on the biochemical process in the soil during the past year will be deferred to the next Report. Although several interesting papers have appeared, the position of the subject has not changed materially during the period under review.

[32] G. W. Robinson and R. Williams, *Trans. Faraday Soc.*, 1924; F. L. Duley, *Soil Sci.*, 1924, **17**, 213. C. O. Swanson, P. L. Gainey, and W. L. Latshaw, *ibid.*, 181; *A.*, i, 820. A. G. McCall, *J. Amer. Soc. Agron.*, 1923, **15**, 290; *A.*, i, 922. Densch, Hunnius, and Pfaff, *Z. Pflanz. Düng.*, 1924, [*B*], **3**, 248. A. Schuckenberg, *ibid.*, 65. D. Drushinin, *Arb. Wiss. Inst. Düngemittel* (*russ*)., 1923, Lief. 20, 1. *Chem. Zentr.*, 1924, i, 1999.

[33] *Ann. Reports*, 1922, **19**, 207; 1923, **20**, 210.

The Chemistry of the Living Plant.

Carbon Assimilation and Photosynthesis.

Baeyer's hypothesis that the first stage in the photosynthesis of carbohydrates from carbon dioxide and water is the production of formaldehyde, which is subsequently polymerised to sugars, still finds acceptance in most quarters. Owing to the experimental difficulties in this field, and to the fact that the process of carbon assimilation consists of a whole series of consecutive reactions which proceed very rapidly, direct evidence of the validity of the hypothesis is lacking, and will probably continue so. In recent years, however, a considerable amount of indirect evidence has been produced which greatly strengthens the probability that Baeyer's hypothesis is the correct one; the investigations of Willstätter and Stoll [34] and of Baly and his co-workers [35] are perhaps the most important in this connexion. The exact mode of production of formaldehyde, however, and the part played by various factors in this process, remain subjects of much speculation and theorising.

Particularly controversial is the question of the part played by chlorophyll in the process. According to the views of Baly, Heilbron, and Barker, the chlorophyll acts as a photocatalytic energy transformer, absorbing radiant energy from the region of the visible spectrum, and radiating energy of infra-red wave-length suitable for the conversion of carbon dioxide (loosely combined with the chlorophyll) into activated formaldehyde. Willstätter and Stoll's hypothesis, which is not incompatible with that of Baly, also regards the chlorophyll molecule as taking an actual part in the chemical transformation of carbon dioxide to formaldehyde, the chlorophyll–carbon dioxide complex being supposed to contain a bicarbonate-like grouping attached to the magnesium atom; this grouping is regarded as changing to a formaldehyde–peroxide complex, which then splits off as formaldehyde and oxygen. Maquenne's view is somewhat similar.[36] Recent work by O. Warburg and T. Uyesugi [37] on the parallelism between the action of hydrogen cyanide and substituted urethanes on the rate of decomposition of carbon dioxide by *Chlorella* and on the decomposition of hydrogen peroxide is held to support the views of Willstätter and Stoll, but it would appear to be equally favourable to any other hypothesis in which the decomposition of a peroxide is an essential feature.

It has long been recognised that there is some other internal factor in the green leaf, associated with the protoplasm, which

[34] *Ber.*, 1915, **48**, 1540; 1917, **50**, 1777.
[35] *J.*, 1921, **119**, 1025. [36] *Ann. Reports*, 1923, **20**, 220.
[37] O. Warburg and T. Uyesugi, *Biochem. Z.*, 1924, **146**, 486; *A.*, i, 922. See also J. Peklo, *Chem. News*, 1924, **129**, 90; *A.*, i, 1018.

regulates photosynthesis; Willstätter and Stoll were compelled to take this into account in the interpretation of their results, and they postulated the existence of a special enzyme which plays an essential part in the assimilatory process. The results recently published by H. A. Spoehr and J. M. McGee [38] indicate that there is present in the leaf something that absorbs carbon dioxide chemically, and that the agent responsible for this is a protein. This conclusion is of interest in connexion with a new hypothesis regarding the mechanism of carbon assimilation, which has been put forward by Wo. Ostwald,[39] and assumes that there is the production of a protein–carbon dioxide compound as the first stage of the process. This is supposed to be accompanied by the autoxidation of a lipoid with the formation of a lipoid peroxide sparingly soluble in water.[40] The protein–carbon dioxide compound and the lipoid peroxide then interact in the presence of water with the production of formaldehyde and oxygen, and the lipoid peroxide is regenerated by autoxidation. According to this hypothesis, the photochemical reaction is not a photo-reduction, but a photo-autoxidation. The whole of the process is supposed to take place at a protein–lipoid interface. An important difference between this hypothesis and that of Willstätter and other workers is that in the new hypothesis chlorophyll takes no part in the actual chemical reaction of conversion of carbonic acid to formaldehyde, but is concerned in promoting the photo-autoxidation of the lipoid.

Although not necessarily supporting the formaldehyde theory of carbon assimilation, the fact that green plants can utilise formaldehyde in low concentrations is of interest as showing that this theory is not incompatible with the anabolic potentiality of the green plant. T. Sabalitschka and H. Riesenberg [41] have supplemented their earlier observations, and those of earlier workers, that green plants can assimilate formaldehyde in the dark with the formation of sugar and starch.

The first products of carbon assimilation the presence of which can be actually demonstrated in the green leaf are carbohydrates. The classical work of Brown and Morris [42] led to the conclusion that cane-sugar was the first recognisable carbohydrate produced by carbon assimilation, and the later work of Davis, Daish, and Sawyer,[43] and of other investigators, lent support to this conclusion.

[38] H. A. Spoehr and J. M. McGee, *Science*, 1924, **59**, 513; *A.*, i, 1392.
[39] Wo. Ostwald, *Kolloid-Z.*, 1923, **33**, 356; *A.*, i, 250.
[40] Compare p. 188.
[41] T. Sabalitschka and H. Riesenberg, *Biochem. Z.*, 1924, **144**, 545, 551; **145**, 373; *A.*, i, 475, 698.
[42] *J.*, 1893, **63**, 604.
[43] *J. Agric. Soc.*, 1916, **7**, 225.

The question has now been reopened by Weevers,[44] whose method of investigation was to study the carbohydrates present in the green and the non-green parts of variegated leaves. He found only sucrose in the non-green parts, but in the green parts he found also monoses. Moreover, when full-grown leaves (of *Pelargonium*) were entirely depleted of sugar and starch by keeping the plants in the dark, and were then exposed to sunlight, the first sugars that could be identified were monoses, sucrose and starch appearing only later. Weevers therefore concludes that monoses are the first sugars to be synthesised during the process of carbon assimilation. It has always been difficult to see why sucrose need be an essential step in the synthesis of carbohydrates by the plant, and confirmation of these results will be awaited with interest.

The investigations of Baly and his co-workers on the photosynthesis of carbohydrates *in vitro* by the action of ultra-violet light on carbonic acid have been carried an important step further by the isolation from the product of methylation of the photosynthetic syrup, by J. C. Irvine and G. V. Francis,[45] of a product that appears to be a tetramethyl hexose. From its amount it appeared that about 10% of the synthesised material consisted of hexose, the bulk of the syrup consisting of non-sugar compounds containing hydroxyl groups.

Synthesis of Polysaccharides in Cereals.

The mechanism of the synthesis of starch in cereals has been the subject of much work and of still more speculation in the past. On the assumption that the building up of starch from soluble sugars passes through the same stages as those observed in the enzymic degradation of starch, the presence of dextrins in the tissues of cereals has been sought for. Some workers (*e.g.*, Péligot, Payen, Hébert) claimed to have found dextrins, whilst others (Dehérain, Müntz) failed to do so. This question has recently been reinvestigated by Belval,[46] who has studied the carbohydrate content of the tissues of various cereals at various stages of maturity. In no case could he find any trace of dextrins, and he advances evidence that the soluble non-reducing substances regarded as dextrins by earlier workers were really mixtures of a lævulosan with sucrose. As a result of his investigations, Belval divides common cereals into two groups. In one group, of which maize is typical, the only

[44] T. Weevers, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 46; *A.*, i, 810.

[45] J. C. Irvine and G. V. Francis, *J. Ind. Eng. Chem.*, 1924, **16**, 1019; *A.*, i, 1286.

[46] H. Belval, "La Genése de L'Amidon dans les Céréales." Nemours, 1924, pp. 1—62; *Rev. gén. Bot.*, 1924, **36**, 308.

soluble carbohydrates found in the stems of the plant during growth are glucose, fructose, and sucrose, that is, the same as are found in the green parenchyma of the leaves. In the other group, to which belong wheat, barley, oats, and rye, there is also found a lævorotatory soluble lævulosan, apparently identical with the "lévosine" isolated from wheat, rye, and barley by Tanret.[47] This substance is found in considerable amount in the stems and grain of the immature plants. Its function is considered to be that of a temporary reserve material, formed at those stages of the plant's growth at which soluble sugars are being produced in the leaves and transported to the developing seeds at a rate greater than that at which the latter can build them up into starch. The plant converts this excess of soluble sugars into the high-molecular polymeride in order to avoid the osmotic disturbances that would ensue if large concentrations of simple sugars accumulated in the tissues. Later on, after the rate of starch formation in the seeds has equalled that of sugar supply to them, this temporary reserve of lævulosan disappears. It is not suggested that this lævulosan is an intermediate step in the building up of starch from soluble sugars. Its conversion to starch in the grain is probably preceded by its hydrolysis to lævulose.

During the germination and malting of barley there is a considerable production of pentosans, which must be formed from the reserve hexosans of the seed, although whether from the starch of the endosperm or from hemicelluloses is not known.[48]

Translocation of Sugars and their Metabolism.

In view of the increasing importance that is being attached to the relation between carbohydrates and phosphates in the transport of calcium in the blood, in ossification, and in the metabolism of carbohydrates in animal tissues,[49] it is of interest to note that recent investigations lay stress on the importance of phosphates in the transport and metabolism of carbohydrates in the plant. Thus, M. H. van Laer and R. Duvinage [50] find that, during the germination of barley, the mobilisation of the carbohydrate reserves is accompanied by a mobilisation of phosphate, so that the phosphorus of the endosperm is rendered soluble and migrates in this form to the embryo. Moreover, the amount of phosphorus thus transported to the embryo is proportional to the amount of growth made by the

[47] *Compt. rend.*, 1891, **112**, 293; *Bull. Soc. chim.*, 1891, [iii], **5**, 724.

[48] M. H. van Laer and A. Masschelein, *Bull. Soc. chim. Belg.*, 1923, **32**, 402; *A*, i, 476.

[49] See p. 202.

[50] M. H. van Laer and R. Duvinage, *Bull. Soc. chim. Belg.*, 1923, **32**, 355; *A.*, i, 250.

latter—a fact which suggests that there is a definite chemical relationship between the migrating sugars and the phosphates. C. J. Lyon,[51] in an investigation of the effect of phosphates in the respiration of *Elodea canadensis*, has found a definite relationship between the rate of respiration and the phosphate concentration of the medium. Here again we have an instance of the importance of phosphates in a process consisting essentially in the oxidation of carbohydrates.

The mechanism of oxidation in the plant is a question the close relation of which to the process of plant respiration is obvious. The oxidising system of the plant is now commonly acknowledged to consist of two components, a peroxide or "oxygenase" and a peroxydase. The chemical nature of these components, and of their interaction forms the subject of three interesting papers by Gallagher.[52] The oxygenase appears to be a lipoid material which is autoxidisable, with the production of a peroxide of the superoxide (Mendeléev) or antozonide (Schönbeim) type ($R<\overset{O}{\underset{O}{|}}$). The peroxydase also appears to be organic in nature, and according to Gallagher's work on the mangold peroxydase, it is derived from an aldehyde. The inactivation of peroxydase by boiling is not accompanied by the loss of aldehyde properties in the preparation, and moreover, the heat-inactivated peroxydase becomes reactivated on standing. Since iron was present in these peroxydase preparations, and since iron salts, when added to aqueous solutions of aliphatic aldehydes, caused an increase in the peroxide activity already exhibited by the aldehyde solutions alone, it is concluded that the zymogen or precursor of the active peroxydase is an aldehyde, which is oxidised, under the catalytic influence of iron, to a peroxide of the polyoxide (Mendeléev) or ozonide (Schönbein) type (R = O). The mode of action of the oxygenase–peroxydase system is then supposed to consist in the combination of the two types of peroxides with the production of a substance with an oxidation potential comparable with that of ozone and higher than that of either of the reactants, this compound being the actual oxidising agent :

$$\underset{\text{Oxygenase.}}{R_1{=}O} + \underset{\text{Peroxydase.}}{\overset{O}{\underset{O}{|}}{>}R_2} \longrightarrow R_1{=}O{<}\overset{O}{\underset{O}{||}}{>}R_2.$$

There are naturally still many points to be investigated before the validity of this hypothesis can be regarded as well established,

[51] C. J. Lyon, *J. Gen. Physiol.*, 1924, **6**, 299; *A.*, i, 476.

[52] P. H. Gallagher, *Biochem. J.*, 1923, **17**, 515; 1924, **18**, 29, 39; *A.*, 1923, i, 1159; 1924, i, 595.

but the results so far obtained are promising, and the further progress of this work will be watched with interest.

Nitrogen Fixation by Green Plants.

In the Report for 1922 reference was made to the publication by C. B. Lipman and J. K. Taylor [53] of a preliminary note in which it was stated that evidence had been obtained for the fixation of atmospheric nitrogen by wheat plants. A detailed account of this work has now appeared,[54] and it is thus possible to examine the evidence carefully.

The analytical data given by Lipman and Taylor with regard to wheat and barley plants grown in liquid culture either devoid of nitrogen or containing varying amounts of nitrate leave little or no room for doubt that there was an actual fixation of atmospheric nitrogen. The authors devote considerable attention in their paper to the question of whether this fixation could have been caused by bacteria in their cultures. They bring forward many arguments in favour of the view that bacterial intervention of this kind cannot have occurred, and they claim that their results "prove that the nitrogen gained by our cultures at the expense of the nitrogen of the air was not first fixed by bacteria and then passed on to the plant. The fixation of nitrogen must have occurred directly, and probably occurs in the cells of the green leaves."

It is not possible here to consider Lipman and Taylor's arguments in detail. Although the cogency of many of these arguments is open to question, they have certainly made out a case. In discussing the merits of earlier work on the same subject, they reject as untrustworthy and inconclusive all earlier work on which claims for the fixation of nitrogen by green plants have been based with the exception of that of Mameli and Polacci.[55] To this work, as well as to that of Lipman and Taylor, the objection still applies that, although it is not possible to affirm that the nitrogen fixation observed was caused by contamination with bacteria, and although Lipman and Taylor have made out a plausible case for thinking that such was not the case in their experiments, the possibility still exists. However strong may be the presumptive evidence in favour of the fixation having been effected actually by the plants themselves, the point cannot be accepted as conclusively proved until experiments have been carried out under conditions excluding the possibility of bacterial intervention. Lipman and Taylor state that

[53] *Ann. Reports*, 1922, **19**, 222.

[54] C. B. Lipman and J. K. Taylor, *J. Franklin Inst.*, 1924, **198**, 475; *A.*, i, 1276.

[55] *Atti Instit. Bot. Pavia*, 1911, **15**, 159.

they are planning further experiments on these lines, the results of which will be awaited with great interest.

Even if we admit the possibilty of nitrogen fixation by green plants such as wheat, it is difficult to suppose that it can be a factor of any economic importance. In Lipman and Taylor's experiments the wheat plants that were grown without the addition of any nitrogen were very stunted; although they remained healthy and continued to form new growth for 24 weeks, there was no comparison between the amount of growth and that given by the plants which received nitrates. Indeed, agricultural experience leaves no possible room for doubt that large and economic yields of wheat cannot be grown unless there is available to the growing plant a sufficient supply of combined nitrogen in an assimilable form. This does not detract from the very great theoretical interest attaching to the possibility of limited nitrogen fixation by green plants, nor from the importance attached by Lipman and Sharp to the cumulative effect that such limited fixation would have, when exerted by successive generations of plants growing under natural conditions, in building up a supply of combined nitrogen and thus in the course of time contributing materially to the nitrogen compounds on the earth's surface.

The Synthesis and Metabolism of Proteins in Plants. The Rôle of Asparagine.

That nitrates are the form in which most plants obtain nitrogen from the soil is well known; ammonium compounds, although they may be absorbed directly by plants, are usually less suitable. This fact is emphasised by the recent experiments of E. B. Fred,[56] who found that when barley was grown in sterile sand cultures in which nitrogen was supplied as ammonium sulphate, the yield obtained and the percentage of nitrogen in the crop were much less than when pure cultures of nitrifying organisms were added to the otherwise sterile sand.

This favoured position of nitrates is all the more difficult to understand when it is remembered that the proteins and other organic nitrogen compounds synthesised by the plant are all derivatives of ammonia, and that therefore in the conversion of nitrates into proteins, reduction of nitrate to ammonia or its derivatives must occur. Why is it that, in order to transform nitrogen from the form of organic derivatives of ammonia in the soil into organic derivatives of ammonia in the plant, it is necessary for ammonia to be oxidised to nitrate in the soil before absorption, only for the process to be reversed, and ammonia derivatives to be reformed in

[56] E. B. Fred, *Soil Sci.*, 1924, **18**, 323; *A.*, i, 1393.

the plant? Not until very much more is known of the chemical processes going on in the living plant will it be possible to answer this question, but it is important to bear in mind that the absorption of nitrate ions implies also the absorption of kations, chiefly $Ca^{\cdot\cdot}$, whereas the absorption of ammonium ions implies the absorption of anions. Investigations of the reaction of plant juices and of the mutual relations of different kations in the nutrient solution and in the plant will probably throw much light on this question; in particular, the *rôle* of calcium in the absorption of nitrogen by the plant and in the synthesis of proteins therein is a fruitful subject of investigation (see p. 195).

According to the hypothesis of Baly, Heilbron, and Hudson,[57] the conversion of nitrates to amino-acids in the plant demands the preliminary reduction of nitrates only to the stage of nitrites. Protein synthesis in the leaf then becomes actually a photosynthetic process in its first stage—the production of activated formaldehyde, which reacts at once with nitrite. Whether this is true, or whether protein synthesis can also go on in the leaf without the intervention of light, is not yet definitely established, but it is certain that the resynthesis of proteins in other parts of the plant, as in the seed, is independent of light, and evidence is accumulating that this synthesis is one in which ammonia and soluble sugars are the initial substances. The occurrence of the same process in the leaf in darkness would therefore appear to be possible.

The power to reduce nitrates through nitrites to ammonia has been found by S. H. Eckerson [58] to be possessed by extracts from various parts of the tomato plant. This reduction occurred actively in the light or in the dark, and also in boiled extracts, provided that a faintly alkaline reaction (p_H 7·6) was maintained. In view of the importance that is being ascribed to iron in the oxidative processes of the plant (see p. 209), it is interesting to note that the results of Eckerson indicate that the presence of iron is also probably an important factor in the nitrate-reducing power of plant extracts.[59]

In recent years, considerable attention has been directed to the occurrence of asparagine in plants and to the part that this substance may play in the translocation of nitrogen and in protein metabolism. A recent paper by H. E. Woodman and F. L. Engledow,[60] in which the development of the wheat grain has been followed with special reference to the synthesis of the proteins of the grain, provides a convenient opportunity for summarising the position of this part

[57] *Ann. Reports*, 1922, **19**, 220.

[58] S. H. Eckerson, *Bot. Gaz.*, 1924, **67**, 377. See also V. L. Anderson, *Ann. Bot.*, 1924, **38**, 699; *A.*, i, 1393.

[59] See also O. Baudisch, *J. Biol. Chem.*, 1921, **48**, 489; *Science*, 1923, **57**, 451.

[60] *J. Agri. Sci.*, 1024, **14**, 563.

of the subject. From the fact that at no investigated stage in the development of the grain could nitrate be detected, it is concluded that the reduction of nitrate to ammonia occurs at some point exterior to the grain, and that the nitrogen for protein synthesis enters the grain either in the form of amide (asparagine) or ammonium compounds or both. Various earlier workers have noted that whenever the amount of protein in leaves underwent diminution, there was a corresponding appearance of asparagine, and it was suggested that asparagine was the nitrogenous substance concerned in the elaboration of protein in the plant. The more recent work of Prianischnikov [61] and of Chibnall [62] has considerably amplified this view. According to Prianischnikov and Schulov, asparagine synthesis occurs in the plant whenever an excess of ammonia is present, caused either by rapid uptake of nitrogen by the roots or by deamination in the plant tissues. Smirnow's [63] work on the metabolism of the lupin embryo has led him to similar conclusions. Prianischnikov draws an analogy between the function of asparagine in the plant and that of urea in the animal organism. In young plants, when protein metabolism gives rise to ammonia, which is toxic if present above a certain concentration, the ammonia is rendered harmless by condensation with aspartic acid to form asparagine. Chibnall has demonstrated the occurrence of the same process in the mature leaf under certain conditions. Plants therefore remove ammonia as asparagine, whilst in the animal it is rendered harmless by conversion into urea.

The analogy must not be pushed too far, however. Urea is a waste product in the animal organism, and is excreted. In the plant, on the other hand, asparagine is a temporary reserve in which form an excess of ammonia may be stored in a harmless and mobile condition, to be utilised for protein synthesis as soon as further supplies of carbohydrate become available from the leaves. Prianischnikov found that in seedlings the amount of asparagine formed was dependent on the amount of carbohydrate available. Excess of carbohydrate led to the conversion of asparagine into amino-acids and proteins, and in the absence of carbohydrates the reverse change took place: protein degradation with the formation of asparagine. Chibnall's results support this view. He finds that asparagine is the chief product of metabolism of proteins in the mature leaf, and he concludes that this type of protein degradation is the chief means whereby the plant is able to convey nitrogen, in a form

[61] M. Prianischnikov and Schulov, *Ber. deut. Bot. Ges.*, 1910, **28**, 253; M. Prianischnikov, *Landw. Vers.-St.*, 1922, **99**, 267; *Rev. gen. Bot.*, 1924, No. 423, 108.

[62] A. C. Chibnall, *Biochem. J.*, 1924, **18**, 387, 395; *A.*, i, 810.

[63] A. Smirnow, *Z. Pflanz. Düng.*, 1924, [*A*], **3**, 30.

suitable for easy resynthesis of protein, from one part of the plant to another. The work of Vickery [64] on the nitrogenous constituents of the juice of the lucerne plant has also shown that asparagine is an important constituent.

Modern work therefore ascribes to asparagine a dual function in the plant: (1) An innocuous storage material for nitrogen, whereby the ill effects of excess of ammonia in the plant are avoided. (2) A mobile form of nitrogen, in which ammonia is transported from one part of the plant to another.

Woodman and Engledow conclude from their results and from the above considerations that nitrogen for protein synthesis enters the developing wheat grain in the form of asparagine derived from protein degradation in the leaves. There is little or no evidence regarding the course of the reactions whereby the asparagine and carbohydrates are converted into protein. These workers believe from their results that ammonia is regenerated from the asparagine, and that ammonia forms the actual starting point of protein synthesis in the grain. There is little evidence for the extensive existence of amides in the plant, and it is suggested as more probable that amino-acids are synthesised from α-hydroxy-acids (produced from carbohydrates) by a reversal of the normal deamination process; in this way, alanine might be formed from lactic acid. Direct experimental confirmation of the occurrence of this process in the plant is lacking.

The subsequent condensation of amino-acids to proteins is readily formulated. The presence of proteoses and of polypeptides in the grain has been demonstrated, and it would thus appear that the building up of proteins from amino-acids goes through the normal stages already familiar in the reverse process of the enzymic degradation of proteins.

Absorption by Plant Roots. "Feeding Power" of Plants.

It is generally supposed that the elements that the plant obtains by means of its roots are absorbed in the form of ions. The conditions determining the rate and amount of absorption of any ion are very complex. A large amount of valuable work is being done on this subject by Hoagland and other workers in California. The time is not yet ripe for a detailed discussion of the results obtained; it may, however, be mentioned that there is definite evidence that the absorption of an ion is influenced by the nature of other ions of the same or of opposite charge, and that the concentration of the solution has an important influence on the magnitude of this effect. Moreover, there is no obvious relation between the ordinary chemical

[64] H. B. Vickery, *J. Biol. Chem.*, 1924, **60**, 647; *A.*, i, 1275.

and physical properties of ions and their rates of penetration into plant cells : the character of the cell membrane must be taken into account. Plant cells may contain ions in far higher concentrations than those in the medium in which they are growing ; it is therefore necessary to take into account the energy relations of the absorption.

It was in view of considerations of this type that A. R. Davis, D. R. Hoagland, and C. B. Lipman [65] took vigorous exception to the hypothesis of Truog [66] on the "feeding power" of plants. Truog believes that the difference between the rate and extent of absorption of essential elements by different types of plant is conditioned by differences in the reaction of the cell sap, and that the relationships involved can be interpreted in terms of the laws of mass action. Davis, Hoagland, and Lipman are of the opinion that Truog under-estimates the fact that differences between the composition of plants may be caused, not by differences in the specific absorbing powers of individual cells, nor yet by the specific reaction of the cell sap, but by the difference in extent of the root system, and the difference in the amount and intensity of carbon dioxide production by roots. They cited the results of Newton [67] in support of this contention. F. W. Parker,[68] who was associated with Truog in the earlier work of the latter investigator on this subject, has now published a paper giving the results of a further investigation on this question. By comparing the amounts of carbon dioxide excreted from the roots of various plants with the absorption of various elements as shown by the composition of the resulting plants, he has shown that there is no relation between carbon dioxide production and the "feeding power" of the plants for calcium, magnesium, phosphorus, and potassium. Buckwheat is a conspicuous example : although the carbon dioxide produced by the roots of this plant was very small, it absorbed a larger amount of these elements than other plants which excreted large amounts of carbon dioxide from their roots. Hence, if we accept Parker's values for carbon dioxide production by plant roots, his results are in favour of Truog's hypothesis to the extent that they indicate that there is some specific difference in plants, apart from the extent of their root system and the excretion of carbon dioxide by their roots, which determines their ability to absorb essential elements from the soil. It must, however, be borne in mind that measurements of the carbon dioxide production in the soil in which plants are growing, as carried out by Parker, are not necessarily a measure

[65] *Science*, 1923, **57**, 299.

[66] E. Truog, *Wis. Agr. Exp. Sta. Res. Bull.* 41, 1916; *Science*, 1922, **56**, 294.

[67] *Ann. Reports*, 1923, **20**, 223.

[68] F. W. Parker, *Soil Sci.*, 1924, **17**, 229; *A.*, i, 811.

of the actual excretion of carbon dioxide by the roots themselves. Different plant roots may give rise to different amounts of organic material to serve as food for soil organisms, which would thus contribute to different extents to the total carbon dioxide produced. It is conceivable that the high production of carbon dioxide in the soil on which plants poor in essential elements (relative to buckwheat) are growing may really be an indication of high bacterial activity in that soil. This high bacterial activity might then result in a high degree of absorption of the elements in question by bacteria, with a consequent diminution in the amount available for the plant.[69] To test that point it would be necessary either to repeat the experiments of Parker in sterile soil, or to include measurements of bacterial numbers and of the concentration of the soil solution in the soil in which the plants were growing.

In general, recent work in this field has laid special stress on the important part played by calcium in the plant. This element is intimately connected with the permeability of plant cells. According to the disputed theory of Truog, calcium is also needed for the neutralisation of organic acids in the plant, and since these acids are supposed to be intimately concerned in the synthesis of proteins, a relation is traced between the amounts of calcium and of nitrogen in the plant. Calcium starvation brings about serious physiological disturbances in the plant. This subject has been studied in California by H. S. Reed and A. R. C. Haas,[70] with special reference to the growth of trees. Trees starved of calcium developed mottled or spotted leaves, which were soon shed, and the trees slowly died. The abnormal mottled leaves had a low content of calcium. The authors direct attention to the similarity between this experimentally produced physiological disturbance and that occurring on citrus trees in the field. Kelley and Cummins [71] have shown that in the latter case the mottled leaves are also deficient in calcium, and that the sap of these leaves contains more than twice as much free acid as that of normal unmottled leaves. Reed and Haas [72] have also shown that the injury to walnut seedlings from solutions of high alkalinity is due not so much to the high hydroxyl-ion concentration in the plant as to the absence of calcium.

Some very suggestive results have been published by Gericke.[73] He found that when wheat plants were grown in solution culture

[69] See *Ann. Reports*, 1923, **20**, 214; see also J. Stoklasa, *Ber. deut. Bot. Ges.*, 1924, **42**, 183; *A.*, i, 1018.

[70] H. S. Reed and A. R. C. Haas, *California Agr. Expt. Sta., Tech. Paper*, 1923, **4**, 21 pp.; *A.*, i, 923.

[71] W. P. Kelley and A. B. Cummins, *J. Agric. Res.*, 1920, **20**, 161.

[72] H. S. Reed and A. R. C. Haas, *Amer. J. Bot.*, 1924, **11**, 78; *A.*, i, 922.

[73] W. F. Gericke, *Science*, 1924, **59**, 321.

in a medium containing all the essential elements, and then after a month were transferred to a solution from which potassium was omitted, the rate of growth and the final yield of dry matter were much greater than those of plants grown throughout in the " complete " solution. In view of the fact that there is some evidence from earlier work that nitrate and potassium are " physiologically paired " ions, that is to say, that nitrate is the anion that predominantly determines the availability of the potassium ion to the cereal plant, Gericke advances the idea that the rapid depletion of nitrate from the soil by the growing plant, as has been demonstrated by the work of Stewart,[74] results in a low availability of potassium to the plant after the initial period of active nitrate absorption, and that this low availability is of advantage, acting to produce increased crops, earlier maturity, and greater vegetative activity, in the same way as when his experimental plants were transferred to the solution deficient in potassium. Gericke has since obtained similar results from the omission of phosphate from the culture solution.[75] The work is yet in its early stage, but the results promise to have an important bearing on the study of crop nutrition.

" *Auximones.*"

A few years ago, widespread interest was aroused by the work of Bottomley on the influence of organic substances on plant growth.[76] Basing his conclusions on experiments in liquid culture with *Lemna*, Bottomley concluded that the green plant needed for its proper growth and development growth-promoting accessory factors similar to the vitamins needed by animals. To these organic substances he gave the name of " auximones." A commercial preparation known as " humogen," or bacterised peat, was put on the market but trials at Rothamsted and elsewhere gave disappointing results. Recently the subject has been investigated by N. A. Clark and E. M. Roller.[77] These investigators found that Bottomley's results could be explained by the fact that the composition of the inorganic culture solution used by Bottomley was not suited to the continued growth of *Lemna*, and that although the addition of peat extract to moribund cultures did cause an increase in the growth rate, it did not nearly bring it back to the initial growth rate in fresh culture liquid free from organic matter. Clark and Roller have utilised a mineral salt solution better suited to the needs of *Lemna*, and by this means they were able to keep the plant growing with unimpaired vigour, and at a rate almost equal to that obtained

[74] G. R. Stewart, *J. Agric. Res.*, 1918, **12**, 311.
[75] W. F. Gericke, *Science*, 1924, **60**, 297.
[76] See *Ann. Reports*, 1916, **13**, 232; 1917, **14**, 232; 1920, **17**, 191.
[77] N. A. Clark and E. M. Roller, *Soil Sci.*, 1924, **17**, 193; *A.*, i, 809.

in the soil, for four months, during which time it passed through more than twenty generations. Whether organic substances exist which can cause a further increase in growth rate in this medium is not yet determined, but it would appear that in any case such substances are not *essential* for the growth and reproduction of *Lemna*, and probably not for any green plants. There is thus no basis for the analogy with vitamins.

Biochemistry of Animals.

Significance of Phosphates in the Cell.

Since the discovery of hexosediphosphate and its *rôle* in alcoholic fermentation by Harden and Young nearly 20 years ago, attention has constantly been attracted, to a greater or less extent, to the relation between phosphates and the sugars in living cells. Many of the views recorded in this field have been highly speculative, and whilst more than one hypothesis has served a useful purpose, they have, as a general rule, lacked adequate experimental foundation. The researches published during the last year or two have provided much that was missing, and the outlook in this quarter is more encouraging than it has been for some time past.

Calcification of Bone and Teeth.

Reference was made in last year's Report to the discovery by Robison [78] of a hexose monophosphoric ester, yielding a soluble calcium salt, which may be hydrolysed by an enzyme present in ossifying cartilage, and it was remarked that the importance of these facts would be far-reaching if it could be demonstrated that such a compound normally exists in the blood. Goodwin and Robison [79] have now produced satisfactory evidence that compounds of this type do occur in the blood, but they have not yet sufficiently purified the isolated substances to establish their actual nature. Two phosphoric esters were isolated, and one of these, showing reducing properties and optically lævorotatory, is hydrolysed by the enzyme found in ossifying cartilage. This is an important observation and greatly increases the significance of the work to which attention was directed last year. If, then, we imagine the calcium phosphate being carried by the blood in this relatively soluble form to centres of calcium deposition, such as the developing bones or teeth, it is necessary to consider the mechanism by which the salt is actually hydrolysed there and the salts are deposited. Papers by Robison and Soames,[80] and Kay and Robison [81] assist us to gain a clearer

[78] *Ann. Reports*, 1923, **20**, 188.
[79] *Biochem. J.*, 1924, **18**, 1161; *A.*, i, 1365.
[80] *Ibid.*, p. 740; *A.*, i, 904.
[81] *Ibid.*, p. 755; *A.*, i, 904.

picture of these changes. The enzyme which hydrolyses the monophosphoric ester is present in bones and teeth and also in the kidneys and intestines. In the young animal, its activity in the first two sites would appear to be more marked than in later life, but its activity in the kidney and intestines seems to be less variable with age. At body temperature, the enzyme shows greatest activity at hydrogen-ion concentrations between p_H 8·4 and 9·4. This fact, together with observations suggesting that in bone the enzyme is normally secreted in the region of the osteoblasts, raises the question whether these cells or the hypertrophic cartilage cells have the power to raise the p_H of tissue fluids. Direct tests indicate that they have this power, but the results are as yet indefinite. In any case, it is necessary to consider the physico-chemical system represented by the calcium compounds present in blood and tissue fluids. It has been known for some time past that a variable proportion of the calcium present in serum will not pass a dialysing membrane.[82] In a recent examination of this matter by Loeb and Steinberger,[83] the proportion passing the membrane was found to be, in some cases, as low as 55% when dialysed against water. When dialysed against 0·8% sodium chloride solution at p_H 7·4, or against hydrochloric acid at p_H 2·5, all the calcium passed through the membrane. These results would appear to indicate an equilibrium between dialysable and non-dialysable calcium in the serum, and are supported by the work of Clark,[84] who found the proportion of diffusible calcium raised after exposure of serum to ultra-violet radiations. Their belief that all the calcium passes through the membrane when dialysis against physiological salt solution is employed, is not in accordance with other results. The general view appears to be that the non-diffusible calcium is in combination with protein. Even if we subtract the amount of calcium present in this condition, there still remains that present in diffusible forms, the concentration of which is considerably greater than that of saturated solutions of calcium carbonate and phosphate. This has led some authorities to view the serum as a metastable super-saturated solution of calcium salts.[85] As Robison and Soames remark: "To consider the plasma as supersaturated with respect to calcium carbonate and phosphate does not seem justified until more is known of the factors influencing the degree of ionisation and the solubility product. A supersaturated solution might, it is true, deposit calcium salts only on coming into contact with the solid phase, *i.e.*, bone, but this would not explain the begin-

[82] A. R. Cushny, *Ann. Reports*, 1920, **17**, 161.
[83] *J. Gen. Physiol.*, 1924, **6**, 453; *A.*, i, 783.
[84] *Amer. J. Hyg.*, 1923, **3**, 481; *A.*, i, 1253.
[85] Rona and Takahashi, *Biochem. Z.*, 1913, **49**, 370.

ning of ossification in embryonic cartilage." If, then, for sake of argument the body fluids be regarded as saturated solutions of calcium carbonate and phosphate, deposition of these salts must occur if the concentration of the ions rises. The concentration of PO_4''' ions will rise if there is an increase in inorganic phosphate, or if there is a shift of p_H towards the alkaline side. Hence the bone enzyme, working between p_H 8·4 and 9·4, if the assumption is allowed that the osteoblasts possess the power to raise the p_H in their immediate vicinity, will cause deposition of tricalcium phosphate. It is interesting to observe that, as the equilibrium between HCO_3' and CO_2 will also be shifted by the change of reaction, there will tend to be deposition of calcium carbonate. On these grounds Robison explains the 10% or so of this substance that is normally found in bone. Bassett [86] has shown that the solid phase in equilibrium with solutions containing calcium and phosphate, under conditions found in normal serum, is hydroxyapatite, $(Ca_3P_2O_8)_3,Ca(OH)_2$, a compound more basic than tertiary calcium phosphate. It is therefore, as Robison points out, surprising that Howland and Kramer,[87] amongst others, should suggest that the solubility product $CaHPO_4$ is the limiting factor in the deposition of bone. Both these workers, as well as Kugelmass and Shohl,[88] have, in their treatments of the subject, regarded the concentration of PO_4''' at p_H 7·4 as so low as to be negligible, and have, without question, been led seriously astray thereby.

The work of Robison and his colleagues has been so carefully controlled at every step, and their results are so unequivocal, that one can scarcely doubt that at last a clear picture is being obtained of the mechanism by which calcium is normally deposited in teeth and bone.

There is little to attract one to the alternative mechanism offered by Freudenberg and György,[89] according to which the physiological fixation of lime takes place in three stages :

Cartilage protein + Ca = Ca–cartilage–protein,

Ca–cartilage–protein + phosphate = Ca–cartilage–protein–phosphate,

Ca–cartilage–preotein–phosphate = calcium phosphate + cartilage protein,

and it is not surprising that this view has been criticised.[90]

[86] *J.*, 1917, **111**, 620.

[87] *Monatsh. Kindersheilk.*, 1923, **25**, 279.

[88] *J. Biol. Chem.*, 1924, **58**, 649.

[89] *Biochem. Z.*, 1923, **142**, 407; *Ergeb. inn. med. Kindersheilk.*, 1923, **24**, 17.

[90] R. E. Liesegang, *Biochem. Z.*, 1924, **145**, 96; *A.*, i, 587.

The other localities where this particular enzyme has been found, namely the intestines and kidneys, suggest that it is there concerned with the absorption and excretion of calcium and phosphates, but this field is as yet unexplored.

Rickets.

The bearing of these studies on ossification on the much debated question of the etiology of rickets is at once obvious, although it is, as yet, not clear how far they enable us to gain a true picture of the abnormalities which characterise this disease.

During the past year further evidence has been forthcoming that normal bone formation will not take place in the absence of an organic constituent of certain normal foodstuffs, which has been provisionally termed vitamin-*D*, or the anti-rachitic vitamin.[91] A deficiency of this dietary factor leads to a fall in the calcium and inorganic phosphate content of the blood, which is made good when the diet is rendered adequate, or, alternatively, when the animal is exposed to ultra-violet radiation.[92] The very surprising experimental results of Hume and Henderson Smith, to which attention was directed in last year's Report,[93] have not been confirmed by Webster and Hill,[94] and at present the whole question of the mode of action of ultra-violet radiation in these cases is in a confused state. It is possible that the remarkable experiments of Steenbock and Black,[95] who found that food deficient in the fat-soluble vitamins may be rendered adequate by exposure to ultra-violet radiation, will do something to clear up the confusion. The results of Clark,[84] referred to above, also strike one as of considerable importance. Meanwhile, it would appear wise to defer further discussion until the matter has received further investigation. However, this brief reference to rickets will serve to connect our discussion of the calcium and phosphoric acid of the blood with another pathological condition that is itself in certain forms associated with rickets, namely, tetany.

Tetany.

Shipley [96] has remarked recently in a valuable review on rickets : "The general character of the relationship of infantile tetany to rickets has become apparent, but the exact nature of the metabolic

[91] Shipley, Kinney, and McCollum, *J. Biol. Chem.*, 1923, **59**, 165, 177; *A.*, i, 685.
[92] Goldblatt, *Biochem. J.*, 1924, **18**, 414; *A.*, i, 788.
[93] See *Ann. Reports*, 1922 and 1923.
[94] *Ibid.*, p. 340; *A.*, i, 340.
[95] *J. Biol. Chem.*, 1924, **61**, 405.
[96] *Physiol. Rev.*, 1923, **3**, 106.

disturbance necessary for the development of tetany continues to remain obscure."

Whilst he is wise in showing caution, we have at least one well-established fact to work upon, namely, that both infantile tetany and that following extirpation of the parathyroid glands are associated with a low concentration of calcium in the blood, and that treatment with calcium salts usually leads to rapid improvement.

Before discussing recent work in this field, it is necessary to refer briefly to the elaborate studies from Professor Noel Paton's laboratory on tetania parathyreopriva which have been fully reported previously in these Reports.[97] Briefly, it may be stated that Paton produced evidence which he regarded as sufficient for concluding that extirpation of the parathyroid glands results in a disorganisation of the mechanism by which guanidine or methylated guanidines produced in the organism are prevented from accumulating. The resulting accumulation of these compounds, possessing as they do a marked action on muscular tissue, was regarded as the chief direct cause of the tetany which follows the removal of the parathyroids. After its publication, Paton's theory was somewhat generally accepted, but it is now being rather vigorously attacked. Perhaps the most serious objections are those raised by Greenwald,[98] who challenges the main statements on which the theory was based, namely, that increased amounts of guanidine and its methyl derivatives are found in the tissues and urine in parathyroid or ideopathic tetany. Greenwald points out that the methods of estimation of these bases employed by Paton's colleagues, Burns and Sharpe, are almost valueless, and that he could not himself obtain any satisfactory evidence that guanidines are present in abnormal amounts after parathyroidectomy. His own conclusions are that the only definite metabolic changes associated with parathyroid tetany are the recognised low calcium content of the plasma or serum and the diminished excretion of phosphates in the urine. This view is supported by other observations on the relation of calcium, and also phosphate, concentration of the blood to tetany. Underhill, Gross, and Cohen,[99] as well as Salvesen, Hastings, and McIntosh,[1] have shown that the administration of large doses of phosphates to dogs induced both tetany resembling parathyroid tetany and the associated fall in the calcium of the serum.

The disappearance of the tetany on administration of calcium salts has always been difficult to explain by the guanidine theory

[97] *Ann. Reports*, 1917, 1918.
[98] *J. Biol. Chem.*, 1924, **59**, 329; *A.*, i, 794.
[99] *J. Metabol. Res.*, 1923, **3**, 679; *A.*, i, 1255.
[1] *J. Biol. Chem.*, 1924, **60**, 311; *A.*, i, 896.

of Paton, and the results of the recent experiments of Palladin and Griliches [2] do not lessen that difficulty.

Of considerable interest, in view of the relation between tetany and rickets, is the observation made by Grant and Gates [3] that considerable hypertrophy of the parathyroid glands has been obtained after 4 weeks' daily radiation with ultra-violet light, whilst Luce [4] found marked hyperplasia of these organs in animals maintained for some time on diets low in calcium.

Disturbances of the calcium phosphate balance in the blood may be readily brought about by injections of one or other component, but the experiments of J. B. S. Haldane, Wigglesworth, and Woodrow [5] show that other factors may cause marked alterations. The alkalosis of forced breathing causes a fall in inorganic phosphate of the blood accompanied by a diminished excretion by the urine, the reverse being true when acidosis is provoked by breathing carbon dioxide or by ingesting ammonium chloride. These results should, however, be considered together with those of Harrop and Benedict,[6] who found that during the active assimilation of carbohydrate there is a fall in inorganic phosphate in the blood and a parallel diminished excretion by way of the urine, as well as those of Wigglesworth, Woodrow, Smith, and Winter [7] demonstrating a similar fall after the administration of insulin. Remembering the hypoglycæmia of parathyroid tetany, the conclusion is justified that the reduction in the phosphates of the blood in these cases is associated with the utilisation of carbohydrate in the tissue-cells.

Phosphates in Carbohydrate Metabolism.

The detection of phosphoric esters of hexoses in blood by Kay and Robison and their isolation in a crude state by Goodwin and Robison have considerably strengthened the position of Embden and his collaborators, who for a number of years past have tended to identify the precursor "lactacidogen" of lactic acid formed during carbohydrate metabolism in muscle with a compound of this type. It will be remembered that Foster and Moyle [8] showed 3 years ago that muscle-tissue possessed the power both to synthesise and hydrolyse "hexosephosphate." Kay and Robison [9] now find that this tissue will only hydrolyse the hexosediphosphoric ester,

[2] *Biochem. Z.*, 1924, **146**, 458; *A.*, i, 898.
[3] *J. Gen. Physiol.*, 1924, **6**, 635.
[4] *J. Path. Bact.*, 1923, **26**, 200.
[5] *Proc. Roy. Soc.*, 1924, [*B*], **96**, 1; *A.*, i, 451.
[6] *J. Biol. Chem.*, 1924, **59**, 683; *A.*, i, 785.
[7] *J. Physiol.*, 1923, **57**, 447.
[8] *Biochem. J.*, 1921, **15**, 672; *A.*, 1921, i, 398.
[9] *Ibid.*, 1924, **18**, 755, 1139, 1161; *A.*, i, 904, 1365, 1368.

the hexosemonophosphoric ester which is so readily hydrolysed by the bone enzyme being unattacked by muscle. Although the experiments are not yet regarded as conclusive, they certainly suggest that there is a hexosediphosphate in the blood; a conclusion which is of interest when one recalls that Emden has long regarded his "lactacidogen" as a hexosediphosphate or a closely-related compound.

Audova and Wagner [10] have reported that following the administration of insulin there is an increase in the "lactacidogen" in the muscles of rabbits, and that the increase is sufficient to account for the dextrose which has left the blood. The importance of this observation is considerable when the uncertainty which still prevails as to the fate of the dextrose that leaves the blood under the action of insulin is borne in mind. Kay and Robison [9] also have studied this matter, and supply confirmation, in so far as they show that the administration of insulin leads to synthesis of organic phosphoric esters. This synthesis occurs in the corpuscles at the expense of the inorganic phosphate originally present *plus* additional phosphate drawn from the tissues.

The nature of these organic phosphates has not been definitely established, but it is believed that sugar or a sugar derivative is present in their molecule. On the assumption that 1 mol. of dextrose combines with 1 mol. of phosphorus, the esterification as measured by the loss of inorganic phosphate would account for approximately 40% of the sugar which simultaneously leaves the blood. An important feature of Kay and Robison's experiments is that allowance was made for the changes in blood volume which may follow insulin administration.[11]

The figure of 40% put forward by Kay and Robison is more reasonable than the suggestion of Audova and Wagner that formation of "lactacidogen" accounts for all the sugar lost, for evidence is accumulating that some of the sugar is oxidised. Thus, in human subjects studied by Perlzweig, Latham, and Keefer [12] the administration of insulin brought about the typical fall in inorganic phosphates in blood and urine and a rise in the respiratory quotient, the latter indicating, in their opinion, increased breakdown of carbohydrate, although Dickson, Eadie, Macleod, and Pember [13] are uncertain how far this rise in the respiratory quotient can be thus interpreted.

An enzyme which can hydrolyse hexosediphosphoric esters is

[10] *Klin. Woch.*, 1924, 3, No. 6; *Compt. rend. Soc. Biol.*, 1924, **90**, 308.
[11] Haldane, Kay, and Smith, *J. Physiol.*, 1924, **59**, 193.
[12] *Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 33.
[13] *Quart. J. Exp. Physiol.*, 1924, **14**, 123.

present not only in muscle-tissue,[14] but also in the corpuscles and plasma of blood.[15] Indeed, the work of Forrai and of Y. Takahashi[16] suggests that similar catalysts have a rather wide distribution in the body. That efficient mechanisms exist in the animal body for converting sugars into phosphoric esters can no longer be doubted. Lawaczeck [17] has studied the dynamics of the phosphates in the blood, but his results are chiefly of importance in stressing the reversibility of the change from inorganic to organic phosphates. That the *rôle* of phosphates is an important one in the metabolism of organisms other than the higher animals is, of course, known from the classic work of Harden and Young on alcoholic fermentation. Additional evidence from other quarters is, however, accumulating. I. S. Maclean and D. Hoffert,[18] in a study of the carbohydrate and fat metabolism of yeast, present evidence that a hexosephosphate may be the first stage in the conversion of carbohydrate into fat. From the work of C. J. Lyon,[19] who records the stimulant action of phosphates on the respiration of the green plant *Elodea canadensis*, and that of M. H. van Laer and R. Duvinage,[20] who think that soluble phosphorus compounds play a part in the transport of foodstuffs in the germinating seed, it is easy to imagine that, before long, to phosphoric esters of sugars will be ascribed as important a part in the metabolism of the higher plants as the *rôle* now allocated to them in animal physiology.

Insulin.

A mass of literature dealing with insulin has accumulated during the past year, but a review of it does not provide much material for this Report. Many of the papers deal with the preparation of the active principle, and numerous new methods or modifications have been proposed. One of considerable value on account of its relative cheapness is that described by Dodds and Dickens.[21] In this method, the macerated pancreas is extracted with aqueous formic acid, and the extract precipitated with picric acid. "Insulin picrate" is extracted from the precipitate by acetone and is treated by Dudley's method.[22] Extraction of the pancreas with sodium

[14] Kay and Robison, *Biochem. J.*, 1924, **18**, 1139; *A.*, i, 1368.
[15] Martland, Hansman, and Robison, *ibid.*, 1152; *A.*, i, 1381.
[16] *Biochem. Z.*, 1924, **144**, 149; **145**, 48, 54; *A.*, i, 456, 594; *ibid.*, **145**, 178; **146**, 161; *A.*, i, 589, 802.
[17] *Ibid.*, 1924, **145**, 351; *A.*, i, 680.
[18] *Biochem. J.*, 1923, **17**, 720; *A.*, i, 352.
[19] *J. Gen. Physiol.*, 1924, **6**, 299; *A*, i, 476.
[20] *Bull. Soc. chim. Belg.*, 1923, **32**, 355; *A.*, i, 250.
[21] *Lancet*, 1924, i, 330.
[22] *Biochem. J.*, 1923, **17**, 376; *A.*, i, 967.

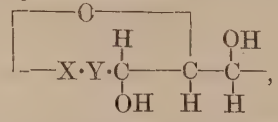
bicarbonate may increase the yield of insulin nearly fivefold.[23] Dudley [24] as well as Vincent, Dodds, and Dickens [25] have found that very high yields of insulin may be prepared from the islet tissue of certain fish, *e.g.*, the cod, in which this tissue lies separate from the glandular organ. This, of course, supports the current opinion that the active principle is secreted by the islet cells. We still remain ignorant of the chemical nature of insulin, in spite of the elementary analysis and molecular formula offered us by at least one enthusiastic worker.[26] The majority of the evidence that has been collected since last year's Report was written supports Dudley's original view that insulin is either a protein derivative (proteose) or an active substance intimately associated with such a compound.

Biological Degradation of Dextrose.

The production of lactic acid as an intermediate product in the breakdown of carbohydrates in muscle is now generally recognised, and we have seen that Embden's view, that its immediate precursor, "lactocidogen," is a hexosediphosphate, has been considerably strengthened by recent studies of the phosphoric esters of the sugars. The intermediate formation of such a compound has always suggested that the combination with phosphoric acid in some way "activates" the sugar molecule, rendering it more readily degraded. Thus Warburg and Yabusoe [27] have recently found that lævulose, but not dextrose, is oxidised in the presence of phosphates by atmospheric oxygen. The action of the phosphates is specific and cannot be replaced by other salts. The theory advanced by Winter and Smith [28] 2 years ago, according to which the normal mixture of α- and β-dextrose is converted into the more reactive γ- or ethyleneoxide form before it is broken down by the body-cells, would appear to have been generally rejected; several other investigators having been unable to confirm their work.[29, 30, 31] Alternatively, we have the suggestions by Laquer and Griebel [32] that α-glucose, or by Thannhauser and Jenke [33] that β-glucose, is the form actually broken down. In both cases, the evidence is obviously insufficient to justify the view put forward. Much more valuable data are

[23] Dudley and Starling, *Biochem. J.*, 1924, **18**, 147; *A.*, i, 585.
[24] *Ibid.*, p. 665; *A.*, i, 897.
[25] *Lancet*, 1924, ii, 115.
[26] Cruto, *Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 42; *A.*, i, 1271.
[27] *Biochem. Z.*, 1924, **146**, 380; *A.*, i, 713.
[28] *Ann. Report*, 1922, 195.
[29] Hume and Denis, *J. Biol. Chem.*, 1924, **59**, 457; *A.*, i, 784.
[30] Denis and Hume, *ibid.*, 1924, **60**, 603; *A.*, i, 1252.
[31] Tallerman, *Biochem. J.*, 1924, **18**, 583; *A.*, i, 897.
[32] *Z. physiol. Chem.*, 1924, **138**, 148; *A.*, i, 1128.
[33] *Münch. med. Woch.*, 1924, **71**, 196; *A.*, i, 897.

advanced in an extensive study of the efficiency of the various sugars and their derivatives in relieving symptoms caused by insulin in mice described by Herring, Irvine, and Macleod.[34] Complete positive results were obtained with dextrose and mannose, also with maltose, but in this case the action was not so prompt. These results with the chief sugars provide confirmation of the results obtained previously by Noble and Macleod.[35] The case of maltose is curious, and it is impossible to say whether hydrolysis to glucose must precede its physiological action. The authors note the interesting fact that both dextrose and mannose are readily fermented by yeast and are also characterised by being the most powerful restoratives of insulin hypoglycæmia. How far this is associated with their ability to form phosphoric esters cannot yet be said. The case of lævulose, however, shows some irregularities, for it is decidedly inferior to dextrose in diminishing hypoglycæmia, but is readily fermented. Among tetramethyl glucose, trimethyl glucose, and tetra-acetyl fructose, only the last one showed any signs of activity. Sucrose, α- and β-methylglucoside, tetramethyl β-methylglucoside, tetramethyl γ-methylglucoside, mannitol, dulcitol, and β-glucosan were all inactive. Salicin gave indications of exercising a slight action, but the experiments were vitiated by its deleterious effect. It is possible that its effect is due to hydrolysis. Reviewing these and other results, Irvine notes that the presence of the reducing group is necessary for activity to be shown. Furthermore, since arabinose shows no activity, it points to the sugars functioning as cyclic structures rather than as aldehydes. We may quote the paragraph: "A review of the combined results shows no exception, which cannot be adequately explained, to the generalisation expressed in the statement that the type of carbohydrate molecule functional in eliminating the convulsion symptoms occasioned by the administration of insulin is



where either X or Y represents a reducing group." Lastly, the absence of action on the part of glucose monoacetone, a readily hydrolysed derivative of γ-glucose, should finally dispel the γ-glucose theory of Winter and Smith.

The curious observation has been recorded by Bodansky and by Ducheneau [36] that the effect of insulin is more profound and pro-

[34] *Biochem. J.*, 1924, **18**, 1023; *A.*, i, 1387.
[35] *Amer. J. Physiol.*, 1923, **64**, 547.
[36] *Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 46.

longed in animals from which the thyroid gland has been extirpated. This has been confirmed by Burn and Marks,[37] who studied the effect of insulin on the same animals before and after removal of the gland. It must be remembered that this operation usually involves removal of the parathyroid glands as well, so that the possibility must be considered whether the effect may not be due, wholly or in part, to the loss of the smaller glands which, as we have seen, may possibly be concerned in carbohydrate breakdown.

The *rôle* of lactic acid in muscular exercise has been the subject of a valuable series of papers by Hill, Long, and Lupton.[38] They are too long for detailed notice here and should be read in the original. One outstanding point may, however, be referred to, namely, their observations, in collaboration with Furusawa,[39] that the respiratory quotient of the total excess metabolism caused by short-lived muscular effort appears to be unity. This is in agreement with Meyerhof's [40] view that the recovery process in isolated muscle has a respiratory quotient of unity. It suggests that after a short period of muscular work the recovery process involves the oxidation simply of lactic acid or carbohydrate.

In relation to this problem is the paper by Foster and Woodrow,[41] who confirm and extend some earlier and interrupted work of Winfield and Hopkins [42] which demonstrated that pancreatic preparations can inhibit the formation of lactic acid in chopped muscle. As the inhibitive substance was found not to be insulin, it was obvious that the authors should recall Dakin and Dudley's antiglyoxalase, but they think the evidence tends to show that its identity does not lie there. Nevertheless the idea that lactic acid arises from methylglyoxal is decidedly attractive and further work should be done. Eadie Macleod and Noble [43] report that, whereas insulin had no action on glycolysis in defibrinated blood, it markedly retarded it in mixtures of blood, muscle juice, and phosphates. Further work would appear to be necessary to clear up the relation of these findings.

Reference was made last year to certain evidence in support of Embden's [44] view that acetaldehyde is an intermediate product in the oxidation of lactic acid to carbon dioxide and water. Simon and Piaux [45] have now shown that lactic esters are oxidised spon-

[37] *J. Physiol.*, 1924, **59**, viii.
[38] *Proc. Roy. Soc.*, 1924, [*B*], **96**, 438; **97**, 84; *A.*, i, 1128, 1362.
[39] *Ibid.*, 1924, [*B*], **97**, 155.
[40] *Pflug. Arch.*, 1919, **175**, 88.
[41] *Biochem. J.*, 1924, **18**, 562.
[42] *J. Physiol.*, 1915, **50**, v.
[43] *Amer. J. Physiol.*, 1923, **65**, 462; *A.*, i, 113.
[44] *Biochem. Z.*, 1912, **45**, 186; 1913, **55**, 335.
[45] *Bull. Soc. Chim. biol.*, 1924, **6**, 412; *A.*, i, 1034.

taneously with the formation of pyruvates, acetaldehyde, and carbon dioxide. Alanine, which stands in close biological relation to lactic acid, yields the same products if oxidation occurs in an alkaline medium at the surface of a catalyst such as finely-divided copper. G. B. Ray [46] also obtained acetaldehyde as an oxidation product of sodium lactate by hydrogen peroxide. Neuberg and Gottschalk [47] also have studied this problem, and by trapping the acetaldehyde as it is formed by means of calcium bisulphite have found that it is produced from glycogen in guinea-pig liver pulp, and that the amount is increased by addition of sugars and certain related substances. In this respect, the mono- and di-hexosephosphates were more active than dextrose or lævulose. Pyruvic acid also gave rise to acetaldehyde when added to rabbit liver pulp. These investigators observed that the addition of insulin increased the production of acetaldehyde considerably.

In this connexion, Toenniessen [48] claims to have shown that a substance present in pancreas, presumably insulin, is necessary for the production of acetaldehyde from lactic acid by chopped muscle. Indeed, this writer would maintain that insulin acts on lactic acid rather than directly on carbohydrates. In support of this view, he argues that all stages in the breakdown of carbohydrates previous to the appearance of lactic acid proceed normally in the absence of the pancreas, but it is questionable whether he is justified in advancing this view. For example, the very careful experiments of Himwich, Loebel, and Barr [49] have shown that, following short periods of vigorous exercise in the moderately severe diabetic, there is a considerable formation of lactic acid without appearance of the acetone substances. Although these patients were not fully diabetic, and therefore were capable of utilising some carbohydrate, the results gave no hint that the diabetic organism is unable to produce lactic acid from carbohydrate or to dispose of it after it is formed.

Glycolysis in Cancerous Tissues.

A number of papers have recently appeared from the laboratory of O. Warburg which report matter possibly of fundamental importance. The method devised for this work is one which will be of great value in studying the respiration and glycolysis in tissues.[50] Working with this technique, Minami [51] has found that the respir-

[46] *J. Gen. Physiol.*, 1924, **6**, 509, 525; *A.*, i, 829.
[47] *Biochem. Z.*, 1924, **146**, 164, 185, 582; *A.*, i, 785, 920.
[48] *Z. physiol. Chem.*, 1924, **133**, 158; *A.*, i, 446.
[49] *J. Biol. Chem.*, 1924, **59**, 265; *A.*, i, 786.
[50] *Biochem. Z.*, 1923, **142**, 317.
[51] *Ibid.*, p. 334.

ation activity of cancer tissue is of the same order as that of an equal weight of normal tissue, but that the glycolytic activity of the former, as measured by lactic acid production, is many times that of the latter. These results have been confirmed by Waterman,[52] who also attempted to induce normal tissues to exhibit the higher glycolytic activity of the cancer cells. Addition of phosphates was without effect, whilst addition of hexosephosphate gave inconclusive results. The addition of an extract of cancer tissue to the medium in which the normal tissues were kept did, however, cause an increased formation of lactic acid. Warburg[53] has shown that whereas the lactic acid produced by normal tissues under anaerobic conditions is to a large extent oxidised when oxygen is admitted, that produced by cancer cells is only to a small extent so removed. This is illustrated by the figures given by him to express the relations between aerobic glycolysis and respiration in tissues; thus, in cancer tissues it is 3–4, in normal tissues 1, and in benign tumours about 1. The most important part of his work is his observation that, if the oxidation processes in embryonic tissues be depressed by small amounts of hydrocyanic acid or by prolonged exposure to nitrogen, the tissues, when placed under aerobic conditions, give values for this relation of the same order as those given by malignant tumours. He advances very tentatively the idea that cancer may arise as a result of a chronic oxygen-starvation, leading certain cells to show the abnormal metabolism. But there is as yet insufficient evidence to accept this view, attractive as it may appear It seems probable, however, that his work will lead to establishing a relation between the rate of growth and the carbohydrate metabolism of tissues.

The Rôle of Iron in Biological Oxidations.

Considerable interest still centres round auto-oxidisable cell constituents containing sulphur in a sulphydryl grouping. Mathews and Walker[54] first drew attention to the great acceleration of the autoxidation of cysteine that is brought about by the presence of traces of iron. Later, Warburg and Sakuma[55] claimed, on the basis of studies of the depression of this process by cyanides, to have shown that the autoxidation is in reality a catalysis by iron with an intermediate iron–cysteine compound playing an essential part. This view is supported by experiments in which the reaction was carried out in quartz apparatus with special precau-

[52] *Arch. Neerland. Physiol.*, 1924, **9**, 573; *A.*, i, 1374.
[53] *Naturwiss.*, 1924, **50**, 1131.
[54] *J. Biol. Chem.*, 1909, **6**, 289; *A.*, 1909, i, 289.
[55] *Pflug. Arch.*, 1923, **200**, 203; *A.*, i, 138.

tions to eliminate traces of that metal. Under these conditions, the rate of formation of cystine from cysteine was found to be very slow indeed. Abderhalden and Wertheimer,[56] whilst admitting the catalytic effect of traces of iron, do not agree with Warburg that it plays an essential *rôle*. They have confirmed Mauthner's [57] observation that cyanides may reduce cystine, and attribute the inhibitive effect of these compounds on the oxidation of cysteine to the reduction preventing the formation of an autocatalytic cysteine-cystine complex.

Harrison [58] has now provided evidence from Hopkins's laboratory that, during oxidation, cysteine and reduced glutathione behave in a similar manner. The results of these experiments, carried out in quartz apparatus and with great care to exclude, as far as possible, traces of iron, support Warburg's view that depression of oxidation by cyanides is due to the formation of a non-catalytic iron compound with cyanogen. Meyerhof, it will be recalled, believed that inhibition of the catalytic action of copper on the oxidation of thioglycollic acid is due to the formation of a copper–cyanogen complex.[60] The amount of metal that will function is extremely small. Mathews and Walker found that the reaction velocity of the autoxidation of cysteine was doubled by the addition of $M/10^5$-ferric chloride, whereas Harrison has found that 10^{-4} mg. of iron caused a marked increase in the oxidation of glutathione.

Robinson [61] has also noted the catalytic effect of blood pigments and certain derivatives in that she found hæmoglobin, methæmoglobin, and hæmin to exert a catalytic action on the autoxidation of linseed oil. The iron-free hæmatoporphyrin was inactive, so that catalytic action of the other substances is ascribed to the iron present in the molecule. In equal concentrations, the iron present as blood pigment is more effective than in the form of an inorganic salt. Curiously, she found that cyanides at a concentration equivalent to the iron present did not depress the rate of oxidation, and it is at present not clear how the results stand in relation to those described above.

Warburg's [62] views on the *rôle* of iron in oxidations have led him vigorously to attack the well-known dehydrogenation theories of oxidation advanced by Wieland. In place of the latter's view that organic oxidations proceed in two phases—first, hydration, followed

[56] *Biochem. Z.*, 1923, **142**, 68; **198**, 122; **198**, 415; *A.*, 1924, i, 12, 11.
[57] *Z. physiol. Chem.*, 1912, **78**, 32.
[58] *Biochem. J.*, 1924, **18**, 1009.
[60] *Pflug. Arch.*, 1923, **200**, 1.
[61] *Biochem. J.*, 1924, **18**, 255.
[62] *Biochem. Z.*, 1923, **142**, 518; *A.*, i, 242.

by loss of hydrogen by interaction with molecular oxygen—Warburg holds that molecular oxygen must first be activated by contact or combination with a catalyst (iron or other substance). Certainly the inhibition of oxidations by cyanides appears to be more readily explained by Warburg's views, since combination of oxygen with the catalyst and its "activation" are prevented.

Hæmoglobin.

Apart from the experimental work which shows that hæmoglobin and related pigments containing iron can catalyse certain types of oxidation reactions, a considerable amount of important work has been reported during the last year or two on other functions of the blood pigment. We may first refer to the long-debated question whether hæmoglobin can act directly as a transporter of carbon dioxide in the blood. It will be recalled that both L. J. Henderson and Hasselbach demonstrated that values for the hydrogen-ion concentration of the blood can be calculated from the equation $c_H = k \cdot p_{CO_2}/v_{CO_2}$, which show good agreement with the observed values. On these grounds they concluded that the combined carbon dioxide of the blood is carried entirely in the form of bicarbonate in ordinary circumstances. On the other hand, other authorities believed that hæmoglobin could enter into combination, either physical [63] or chemical,[64] with carbon dioxide and thus effect its transport. A recent critical re-examination of the Henderson-Hasselbach equation [65] in its relation to blood has, however, shown that their view is best in agreement with facts. Positive proof that in ordinary circumstances hæmoglobin exists in the corpuscle as the sodium or potassium salt has been forthcoming, for Taylor [66] has made a study of the potential difference between blood or laked corpuscles and salt solution and finds that in all cases the sign of the potential difference indicates that the hæmoglobin is present as an anion. It is, therefore, impossible for hæmoglobin to combine chemically with carbon dioxide until the reaction is brought to the acid side of the isoelectric point of the protein, which is given as p_H 6·8—6·7.[67, 68] Such was actually the case in the experiments of Zuntz in 1883, and in those of Buckmaster in which high pressures of carbon dioxide were employed, but this would not

[63] Bayliss, *J. Physiol.*, 1919, **53**, 162.
[64] Buckmaster, *ibid.*, 1917, **51**, 105, 164.
[65] Warburg, *Biochem. J.*, 1922, **16**, 153.
[66] *Proc. Roy. Soc.*, 1924, **96**, [*B*], 383.
[67] Osato, *Biochem. Z.*, 1922, **132**, 485.
[68] Hastings, Van Slyke, Neill, Heidelberger, and Harington, *J. Biol. Chem.*, 1924, **60**, 89; *A.*, i, 1008.

occur under physiological conditions. It can be seen from this work that sodium or potassium hæmoglobinate must act in the body as a very efficient "buffer," and that base is lost to carbon dioxide with the formation of the free acid :

$$NaHb + H_2CO_3 = NaHCO_3 + HHb.$$

The acid nature of hæmoglobin has attracted wide attention. The demonstration that oxygenated blood is more acid than reduced blood has not been easy because of the difficulty of measuring the small changes concerned. Actual measurements have been made, such as those of Parsons,[69] and although the differences are small they are definite. A. V. Hill [70] has, however, pointed out that the known effect of acid on the dissociation curve of blood makes it thermodynamically inevitable that oxygenation will raise the hydrogen-ion concentration. Further, the effect of carbon dioxide on the dissociation curve, which Barcroft and Murray have shown is due to change of c_H, makes it certain that there will be a corresponding effect on the combination of carbon dioxide. It follows that the effect of oxygenation on carbon dioxide combination must be due to the liberation of a fixed acid about as strong as carbonic acid. What must be regarded as conclusive proofs of this are given in Hill's paper. The same occurs when hæmoglobin combines with carbon monoxide.[71] Hastings, Van Slyke, Neill, Heidelberger, and Harington [72] have directly determined the base-binding power of oxy- and reduced hæmo-globin over the p_H range 6·8—7·6. The increase in base-binding power caused by oxygenation of hæmoglobin has a maximum value of about 0·7 equivalent of base per atom of iron in the pigment, and follows a curve consistent with Henderson's [73] hypothesis that combination with a molecule of oxygen increases the dissociation constant of one labile carboxyl group in the hæmoglobin molecule. It does not follow the equation required by Hill's hypothesis,[74] according to which only one hydrogen atom in an aggregate of n molecules, where n is the index in Hill's oxygen dissociation equation, has its dissociation constant affected by oxygenation or reduction.

$$H(Hb)_n + nO_2 \rightleftharpoons H(HbO_2)_n$$
$$H(HbO_2)_n \rightleftharpoons H + (HbO_2)_n$$

Brown and Hill believe the value of n to be about 2·2. Before leaving this side of the hæmoglobin question attention should be

[69] *J. Physiol.*, 1917, **51**, 440. [70] *Biochem. J.*, 1923, **17**, 544.
[71] Hastings, Sendroy, Murray, and Heidelberger, *J. Biol. Chem.*, 1924, **61**, 311; *A.*, i, 1251.
[72] *Ibid.*, 1924, **60**, 89; *A.*, i, 1008. [73] *A.*, 1920, i, 403.
[74] *Proc. Roy. Soc.*, 1923, [*B*], **94**, 297; *A.*, 1923, i, 398.

directed to an important paper by Henderson, Bock, Field, and Stoddart [75] on blood as a physicochemical system. All the known phenomena of the respiratory cycle have been described with a good approach to accuracy with the following seven variables: free oxygen, total oxygen, free carbon dioxide, total carbon dioxide, p_H of serum, volume of corpuscles, and the ration of the concentrations of anions within and without the corpuscles. This paper merits very careful study.

We may now turn to some very important researches from Barcroft's laboratory. It has long been known on the basis of evidence—chemical, physiological, and serological—that the hæmoglobins of different species are different substances. Most interesting results have followed the efforts of Anson, Barcroft, Mirsky, and Oinuma [76] to correlate the spectra of various hæmoglobins with their relative affinities for oxygen. If the position of maximum intensity of the α-oxyhæmoglobin band, measured in Ångström units, be for any one species A, and that of the corresponding carbon monoxide compound be B, then the shift of the band caused by conversion of the oxyhæmoglobin into carboxyhæmoglobin is A—B, which is termed the "span."

Now if the "span" be plotted against log K, where

$$K = \frac{[\mathrm{HbCO}][\mathrm{O_2}]}{[\mathrm{HbO_2}][\mathrm{CO}]},$$

one obtains practically a straight line, and the relationship may be expressed as log $k = 0{\cdot}05(A—B)$. This means that the displacement of the band corresponds with a proportional change in the free energy of the reaction.

If, now, the relationship between the absolute position of the α-band and the absolute value of the equilibrium constant K be studied, then log K is found to alter by 0·055 for every Ångström unit. Further, if the shift of the band towards the violet that occurs with a fall of temperature be observed, it is found that the alteration in the affinity for oxygen, as measured by the reciprocal of the concentration of oxygen present when half the hæmoglobin is oxidised and half reduced, can be represented by log $1/C_{50\%} = 0{\cdot}049$ for 1 Ångström unit. These three values, showing so close an agreement, obviously represent more than a haphazard coincidence, and indicate that we may be on the point of discovering some fundamental energy relationships of the hæmoglobins.

Incidentally, it may be stated that Barcroft and his colleagues have reasons for believing that the differences are in no small part,

[75] *J. Biol. Chem.*, 1924, **59**, 379; *A.*, i, 780.
[76] *Proc. Roy. Soc.*, 1924, [*B*], **97**, 61; *A.*, i, 1363.

or perhaps entirely, due to the protein moiety, globin. If so, the nature of the protein bound with the hæmatin would appear profoundly to affect the gas-binding powers of the pigment. The conception that the specific characteristics of hæmoglobins are bound up with the protein rather than with the pigment nucleus has been advocated for some time by Vlés,[77] and this recent work would appear strongly to support his view. Furthermore, such a view is more in keeping with our knowledge of the chemistry of hæmoglobin and of the proteins generally. Further work in this field will be awaited with great interest.

Proteins and Amino-acids.

No outstanding work has marked the past year's researches in the field of protein chemistry, but steady, if slow, progress may be recorded.

The preparation of substituted proteins by such processes as bromination, methylation or benzoylation [78] may possibly be of value in throwing light on internal structure, but the results so far achieved do not appear very encouraging. The methylated products are more resistant to attack by erepsin than the parent proteins, and Imai [79] suggests this may be due to the inhibitive effect of methyl groups near the peptide linking.

Experiment on the betaines of glycylglycine, diglycylglycine, and triglycylglycine are described in support of this idea, the first two being unattacked, whilst the last, in which the methyl groups are furthest removed from a peptide linking, is hydrolysed to a slight extent. Similar experiments were made with benzoyl derivatives, but their value is limited by the fact that it is uncertain which peptide linkings were broken.

More valuable data are being obtained from a careful study of the intermediate products in the hydrolysis of proteins.

In referring to the hydrolysis of proteins, passing reference may be made to the statements of Clifford that a catalyst is present in muscle (cod) which can accelerate the hydrolysis of protein at temperatures of 95—100°. Apparently control of the reaction of the medium was not maintained in her experiments, and further data are obviously called for. It has been known for many years that prolonged digestion of proteins, particularly caseinogen, with trypsin fails to give complete hydrolysis. Luck [80] has now observed that the undigested residue totally resists attack by trypsin and that,

[77] *Arch. Phys. biol.*, 1922, ii, 22.
[78] Vandevelde, *Rec. trav. chim.*, 1924, **43**, 158; *A.*, i, 678.
[79] Imai, *Z. physiol. Chem.*, 1924, **136**, 173, 188, 192, 205; *A.*, i, 920, 921.
[80] *Biochem. J.*, 1924, **18**, 669, 679; *A.*, i, 904, 891.

after acid hydrolysis, it consists almost entirely of lysine and glutamic acid. About 10% of the total nitrogen can be liberated as ammonia, and since there is evidence that this is not associated with the lysine, it is concluded that the product is probably a glutamine-containing peptide. Whether glutamine or this complex is present in the caseinogen molecule, or whether it is a secondary product arising by enzymic synthesis, is not yet clear. Fränkel, Gallia, Liebster, and Rosen [81] have isolated a number of substances from caseinogen after digestion with trypsin for two months. A number of the products, such as *d*-tryptophan and *d*-leucine anhydrides, are regarded as arising by secondary reactions. Leavenworth,[82] having studied the basic amino-acids of casein, draws the conclusion that it is improbable that this protein contains any hitherto unidentified member of that group.

Abderhalden [83] and his colleagues continue to carry out long and careful examinations of the products isolated from the partial hydrolysis of proteins. A number of anhydrides of amino-acids have been isolated and identified. He believes that the protein molecule may contain anhydride-like residues having the diketopiperazine structure as well as the recognised peptide chains.

The general method employed to isolate these products of partial hydrolysis has been fully described.

The suggestion of anhydride groupings has arisen also in a new direction from the work of Brill,[84] who has studied the investigation of physical structure of silk-fibroin by *X*-ray methods. He concludes that this product is a mixture of two proteins, of which one is crystalline, and it is suggested that the molecule is composed of alanine and glycine in equimolecular proportions, possibly united in a ring formed of four *d*-alanylglycine anhydride groupings combined as a polypeptide.

In the field of the amino-acids we welcome the valuable method for the preparation and determination of arginine which we owe to Kossel and Gross.[85] Arginine yields an almost insoluble salt with "naphthol-yellow-S," 2 : 3-dinitro-1-naphthol-7-sulphonic acid, which is easily prepared, isolated, and estimated. Karrer [86] has studied the official configuration of the amino-acids, based on *d*-serine, and finds that *d*-alanine, *l*-serine, *l*-cystine, *l*-asparagine, and *l*-aspartic acid all have the same configuration. He suggests

[81] *Biochem. Z.*, 1924, **145**, 225; *A.*, i, 677.
[82] *J. Biol. Chem.*, 1924, **61**, 315; *A.*, i, 1362.
[83] *Z. physiol. Chem.*, 1923, **131**, 284; 1924, **136**, 134; **139**, 181; *A.*, i, 227, 890, 1361.
[84] *Annalen*, 1923, **434**, 204; *A.*, i, 102.
[85] *Sitzungsber. Heidelberg, Akad. Wiss.*, 1923, [*B*], 1; *A.*, ii, 211.
[86] *Helv. Chim. Acta*, 1923, **6**, 957; *A.*, i, 151.

that all naturally occurring amino-acids belong to the same group.

Abderhalden and Sickel [87] have described the isolation of an amino-acid from caseinogen which is regarded as the hydroxytryptophan described by Abderhalden and Kempe in 1907.[88]

Little further information has been forthcoming regarding the structure of the new amino-acid, $C_5H_{11}O_2NS$, isolated by Mueller [89] 2 years ago. Apparently the sulphur is present in a form which is not liberated as hydrogen sulphide on treatment with alkalis.[90]

After administration to man the sulphur is excreted in the urine as inorganic sulphate.[91]

Regarding the physiological significance of the individual amino-acids, we have two papers of interest. One is by Sure,[92] claiming that proline is an essential constituent of the diet for growth in rats, and that substitution of pyrrolidonecarboxylic acid for this amino-acid was not of any value. The other is by Rose and Cox,[93] describing experiments on the relation of histidine and arginine to growth. It will be recalled that Ackroyd and Hopkins [94] found that either one of these two amino-acids must be present in the diet for growth to occur in young rats, but that they are interchangeable. The change was related by these authors to a general similarity of the structure of the two molecules. Rose and Cox now give confirmation of the essential nature of histidine, but cannot agree that histidine in the diet can be replaced by arginine. Progress in study of the metabolism of amino-acids may be illustrated by one or two selected papers. Further confirmation of the oxidation of amino-acids by atmospheric oxygen at the surface of charcoal, originally noted by Warburg,[95] has been advanced by Wieland and Bergel.[96] Glycine, alanine, and phenylalanine yield carbon dioxide and ammonia in equimolecular proportions, an aldehyde with one carbon atom less than the original substance, and a little of the corresponding acid. Somewhat similar results were obtained by Fichter and Kuhn [97] in the oxidation of amino-acids by means of

[87] *Z. physiol. Chem.*, 1924, **138**, 108; *A.*, i, 869.
[88] *A.*, 1907, i, 808.
[89] *Proc. Soc. Exp. Biol. Med.*, 1922, **19**, 161.
[90] *J. Biol. Chem.*, 1923, **55**, *Proc.* xv; **56**, 157.
[91] *Ibid.*, 1923, **58**, 373; *A.*, i, 438.
[92] *Ibid.*, 1924, **59**, 577; *A.*, i, 787.
[93] *Ibid.*, 1924, **61**, 747; *A.*, i, 1370.
[94] *Biochem. J.*, 1916, **10**, 551; *A.*, 1917, i, 237.
[95] *Ann. Report*, 1923, 193.
[96] *Annalen*, 1924, **439**, 196; *A.*, i, 1216.
[97] *Helv. Chim. Acta*, 1924, **7**, 167; *A.*, i, 379.

hydrogen peroxide. Probably both these studies have a close bearing on the mechanism of amino-acid breakdown in the living cell, although the intermediate steps in both cases are not yet known.

For some time, chiefly as a result of Neuberg's and of Dakin's studies, it has been accepted that deamination normally represents the first stage in the breakdown of amino-acids in the organism. This may occur in one of three ways :

(1) by oxidation, with formation of an α-ketonic acid.
(2) by reduction, with formation of a saturated acid, and
(3) by hydrolysis, with formation of an α-hydroxy-acid.

Generally speaking, as Dakin has shown,[98] the evidence favours the first process, with possibly a hydrated imino-acid or a glyoxal derivative at the intermediate product. Fearon and Montgomery [99] now deal with these theories rather critically in directing attention to Werner's [1] view that there are difficulties in accepting the idea of the production of ammonia from the oxidation of an amino-acid in neutral or, more particularly, in alkaline solution.

These authors were able to detect cyanic acid among the products of oxidation of glycine and alanine by hydrogen peroxide, and suggest that the reaction in neutral solution might be written :

$$\begin{matrix} R{-}CH{-}NH_3 \\ | \quad\quad | \\ CO{-}O \end{matrix} + O \longrightarrow R{\cdot}CHO + H_2O + HNCO.$$

Ammonia and carbon dioxide would then arise by hydrolysis of the cyanic acid, and urea would be formed from combination of the acid with ammonia.

It is true that these suggestions bring the mechanism of deamination into line with Werner's well-known views on cyanic acid and urea.[1] Furthermore, they fit in reasonably well with the results of Wieland and Bergel reported above. Where difficulties arise is in reconciling a theory, in which deamination involves nitrogen leaving the molecule with an attached carbon atom, with much that has been accepted regarding the simple transformations that appear to occur in living cells.

How, for example, are we to view it in the light of the very simple change studied by Dakin and Dudley,[2] according to which the α-amino-acids are in equilibrium in solution with ammonia and the α-ketonic aldehydes.

$$R{\cdot}CH(NH_2){\cdot}CO_2H \rightleftharpoons R{\cdot}CO{\cdot}CHO + NH_3.$$

[98] "Oxidations and Reductions in the Animal Body," London, 1922.
[99] *Biochem. J.*, 1924, **18**, 576; *A.*, i, 898.
[1] "Chemistry of Urea," London, 1923.
[2] *J. Biol. Chem.*, 1913, **14**, 555; **15**, 127.

It is doubtful whether Fearon and Montgomery have yet produced sufficient evidence to disturb the views currently held, but their work is suggestive and stimulating.

Uric Acid.

Work in the field of purine metabolism has produced at least one outstanding paper during the last year, namely, that recording an experimental study of the uric acid problem with reference to animals and man, including gouty subjects, carried out by Otto Folin and his co-workers, Berglund and Derick. This publication is one of more than one hundred pages and well repays careful reading.[3]

About 20 years ago, vigorous discussion centred round the question whether or not the human organism can break down uric acid. Burian and Schur's classic work may be regarded as the central point of the defence of those who believed that uric acid is oxidised in human tissues, whereas Wiechowski was one of the chief opponents of this view. The careful review of the literature which prefaces Folin's paper makes it very clear how misleading much of the earlier literature has proved, and how difficult it has been to form an opinion of any value from that mass of conflicting evidence.

The first experiments described were carried out on dogs, which, as was already known, possess the power to oxidise uric acid, in order to learn the immediate distribution in the tissues of injected uric acid. These experiments yielded striking results showing that, of the organs investigated, only the kidneys take up any appreciable amount of uric acid from the blood, and that they may absorb quantities which appear extraordinarily large. It is conceivable, of course, that the other tissues, particularly the liver, which is believed to contain uricase, might also absorb the acid, but that extremely rapid oxidation might render this difficult to detect. The authors present reasonable evidence, however, that such is not the case, and that tissues other than the kidney are actually impermeable to uric acid during life.

The second surprising feature of these experiments on dogs is that uric acid is not destroyed appreciably in the kidneys, but that it very rapidly disappears from the blood, presumably by oxidation. As much as 70% may be destroyed within the first 10 minutes after injection. This destruction ceases as soon as the blood is withdrawn from the circulation and cannot therefore be ascribed to the presence of a uricolytic enzyme in the blood. Folin and his colleagues suggest that an essential part may be played by some factor poured into the blood from some other tissue. As the concentration of

[3] *J. Biol. Chem.*, 1924, 60, 361.

uric acid falls in the blood, the store in the kidney is slowly discharged. The speed of destruction is governed by the concentration in the blood.

Folin confirms the curious fact discovered by S. R. Benedict [4] that the Dalmatian hound shows, as compared with other species of dogs, much slower oxidation of uric acid. It may be of interest to note, in passing, that Onslow [5] investigated the relation between uric acid excretion and allantoin excretion in hybrids of the Dalmatian coach-hound and found that the excretions of the hybrids resemble those of the normal dog. The greater power of destroying uric acid tends to be a dominant character. Returning to the experiments of Folin, Berglund, and Derick, we find that somewhat similar results were obtained with goats, cats, rabbits, and birds, but the speed of destruction was usually very much slower than in the dog.

The experiments with men are perhaps the most important part of the paper, for they do provide us with the first clear-cut evidence that uric acid is broken down in the human organism. Intravenous injection of uric acid (20 mg. of lithium urate per kilo. of body-weight) results in a rapid and prolonged rise in the concentration of uric acid in the blood. From the experiments on other species, and from the fact that the amount in the blood shows very little decrease in a short while after injection, it is concluded that the human organs, other than the kidney, are impermeable to uric acid. From 30—90% is excreted by the kidney, but evidence is presented that from 10—70 (average value 50) % is destroyed. The high levels of uric acid in the blood are regarded as indicating a lack of responsiveness on the part of the human kidney. There appears to be a greater response if the uric acid is administered when the subject is on a high protein dietary, and it is suggested that this is the explanation of the fact that more endogenous uric acid is excreted on a diet rich in protein than on one deficient in that respect. Experiments with subjects prone to gout lead Folin and his co-workers to believe that in this disorder the organism possesses normal powers of destroying uric acid, but that the responsiveness of the kidney to excretion is subnormal and results in maintenance of high uric acid concentrations in the blood.

J. C. Drummond.
H. J. Page.

[4] *J. Lab. Clin. Med.*, 1916, **2**, 1. [5] *Biochem. J.*, 1923, **17**, 334, 564.

CRYSTALLOGRAPHY.

The science of crystallography, as soon as its devotees realised that in the method of *X*-rays they possessed a crucial test for its long-neglected geometrical theory, came in one stride into its own. It has emerged triumphantly from this trial and now advances with that rapidity which is to be expected only from a science which applies a sound technique to the needs of a trustworthy theoretical treatment. We feel quite sure now of what we have to look for in the inner structure of crystals, and this knowledge, supplemented by the mass of evidence known to the neighbouring sciences with which crystallography is fast becoming closely involved, will help us soon, there is no doubt, to play an all-important part in the quest of the nature of the atom. In the last few years the theory of space-groups has attained a highly satisfactory position. Through it crystallography has acquired the means of furnishing first-rate information on dubious points of both chemistry and physics, for it is only from crystals that we can get a clear idea of what atoms and molecules will do when comparatively free from such powerful disturbing factors as prevail in the liquid and gaseous states. In some ways this may appear a disadvantage, but on the whole the results will be highly acceptable. It is not easy to believe that in crystals the atomic configurations are very different from what we should expect in "free" molecules—no doubt there are small differences, but they are so small as to detract only a little from the value of the conclusions. Crystals are not "dead"; rather shall we say they are only "quietened down" somewhat.

Last year, R. W. G. Wyckoff gave us a complete analytical expression of the theory of space groups—an invaluable work. This year,[1] the subject has been approached from a different point of view, one which we venture to hope will prove intelligible and immediately useful to physicists and chemists even of negligible training in mathematical crystallography. A simple principle has been used to deduce the abnormal spacings to be expected from each of the 230 space-groups when examined by *X*-rays, thus providing a complete list to which reference can be made with great facility. Together with this table are given all the possible molecular (and therefore ionic and atomic) symmetries

[1] W. T. Astbury and K. Yardley, *Phil. Trans.*, 1924, [*A*], **224**, 221; *A.*, ii, 720.

for all possible cases, a list which, we trust, will appeal strongly to chemists. Finally, diagrams are given showing in the simplest possible manner all the 230 ways in which molecules can unite to form the various types of crystal-structure. With the aid of these the crystal-analyst can readily form a mental picture of what sort of combination he is dealing with. To many—this seems to be characteristic of the science of our own country—such an opportunity is always desirable.

Metals, Alloys, etc.

The study of the crystalline structure of metals, alloys and intermetallic compounds is at the same time one of the most important and difficult branches of crystallography. Its material usefulness is manifest, yet from the point of view of pure science also the lessons to be drawn from the study of such substances are full of significance for many of the baffling problems of atomic physics. It is essential, before these problems can be attacked profitably, that the data should be as well defined as possible, that crystalline structure should be known down to the individual atomic positions. When this knowledge has been gained for a large number of metals and alloys, we shall have made an enormous advance towards our goal.

Unfortunately, our present knowledge of the inner structure of alloys can only be described as scanty. The problem is so full of pitfalls that it is useless to approach it with any but the most carefully organised plans, prepared in collaboration by metallurgist, physicist, chemist, and crystallographer. The trouble so far is that this has not been done, that the investigations have been carried out with insufficient knowledge of some aspect or other of the problem. It cannot be too strongly urged that, if success is to be attained, the closest association must always be maintained between all branches of the subject.

Of this year's work on alloys, probably the investigations which most satisfy these conditions are those of Westgren and his associates. At the May meeting of the Iron and Steel Institute were described some results supplementary to their previous work on the structure of iron and steel. A new photograph of iron at 1450° was decisive that the δ-phase has the same structure as the α-phase, whilst Laue, rotation, and powder photographs of cementite combine to show that the cell is orthorhombic, contains four molecules of Fe_3C, and has the dimensions 4·518, 5·069, and 6·736 Å.U. Cementite has the same structure as cohenite, the iron carbide occurring in meteorites. New photographs of austenite show that austenite increases in size with increase of carbon content

and that the carbon atoms do not replace the iron atoms, but *are situated in the interstices of the face-centred cubic lattice.* On the other hand, a recent investigation (by the ionisation-spectrometer alone) of the structure of hard steel [2] has furnished some evidence that in martensite we have carbon atoms *replacing* iron atoms, after the manner of what has been found to hold in many non-carboniferous alloys such as copper–aluminium, where the individual metals replace each other, atom for atom. For 0·80 and 1·31% carbon steels, both in coarse and fine martensite condition, the same lines were found as in the spectrum of carbon-free iron, but they were only one-third as intense, broader, and slightly shifted. The author concludes that martensite is a mixture of (1) a solid solution of carbon in iron, the C-atoms replacing the Fe-atoms, and (2) finely dispersed cementite, the former contributing to the hardness through distortion and the latter through being so fine-grained.

At the March meeting of the Institute of Metals, E. R. Jette, G. Phragmén, and A. F. Westgren contributed a paper on the structure of the copper–aluminium system. The same system was investigated by Owen and Preston last year, but these more recent results indicate that their work was incomplete, in the sense that with alloys the spectrometer method which they used is not capable of revealing the nature of the large number of planes which must be examined before we can be really sure that we have determined the true cell and space-group. The work of Jette, Phragmén, and Westgren, however, was carried out with all the resources of the various *X*-ray methods, and in consequence it appears to be one of the most trustworthy investigations on alloys yet made. The photographs reveal at once the existence of four different phases, agreeing in the main with the equilibrium diagram of Carpenter and Edwards: (1) α — 7% Al gives displaced Cu lines; 12·5% is a mixture of the α- and γ'-phases: (2) γ' — 16—25% Al gives pure γ': (3) 42% Al gives a mixture of γ' and δ; pure δ at 46% Al: (4) 55, 80, and 95% Al show δ mixed with pure Al. With regard to the δ-phase, $CuAl_2$, Laue, rotation, and powder photographs agree in assigning a body-centred tetragonal lattice, $a = 6{\cdot}05$ and $c = 4{\cdot}88$ Å.U., of which the symmetry is D_{2d}, D_4, C_{4v}, or D_{4h}; four molecules of $CuAl_2$ per cell. This differs from the simple structure proposed by Owen and Preston, and must supersede it.

Laue photographs of the γ'-phase showed cubic symmetry (T_d, O, or O_h), the side of the cell being about 9 Å.U. Exact measurements showed that, whereas Al increases the Cu-lattice in the

[2] K. Heindlhofer, *Physical Rev.*, 1924, **24**, 426; *A.*, ii, 863.

α-phase, it actually *decreases* it from 8·701 (16%) to 8·656 (25%) in the γ′-phase. Furthermore, whilst the α-phase is a case of simple substitution with approximately four atoms per cell, it seems to require 52 to 49 atoms to fill the unit cell of the γ′-phase, corresponding to such formulæ as $Cu_{36}Al_{16}$, $Cu_{33}Al_{18}$, $Cu_{30}Al_{20}$, and $Cu_{27}Al_{22}$. The curve of changing density is in closest agreement with that obtained by supposing that three copper atoms are replaced by two aluminium atoms. This is a truly astonishing state of affairs, and its full meaning is at present quite beyond any conjecture. Curiously enough, no difference can be observed between the relative intensities of the lines in the powder photographs of the 16% and 25% alloys. It is evident that a long and careful inquiry must yet be made into the structure of such a phase before we can feel on safe ground. The elucidation of this problem is of vital importance to the study of the nature of alloys. The photographs of the 95% alloy are practically identical with that of pure aluminium. That of a quenched 12·5% aluminium alloy showed lines corresponding to a phase stable only at higher temperatures.

Of other work on alloys we may mention an *X*-ray examination [3] of mixed crystals of tungsten and molybdenum (50%), and of silver and gold (25 and 75%), which failed to support Tammann's theory that in such mixed crystals the atoms are always located in certain definite places in the space-lattice; and an examination of certain amalgams,[4] the results of which indicate, for tin, zinc, and cadmium amalgams, the appearance in each series of a second type of crystal as the percentage of mercury increases. It seems probable from the powder reflections that the new lattices are hexagonal and different from those possessed by tin, zinc, or cadmium at the ordinary temperature. In the series of lead amalgams, it was found that the presence of 0—20% of mercury atoms contracts the face-centred lead cube by 0—0·08 Å.U.

Of the intermetallic compounds should he noticed Mg_2Sn [5] and Mg_2Si,[6] both of which have been found to possess the "fluor-spar structure," with cube sides 6·78 and 6·39 Å.U., respectively. AlSb [6] is like zinc blende, with side 6·126 Å.U.

Hassel and Mark,[7] by the rotation method, have confirmed the structure of bismuth previously found by other workers,[8]

[3] A. E. van Arkel, *Physica*, 1924, **4**, 33; *A.*, ii, 618.
[4] C. v. Simson, *Z. physikal. Chem.*, 1924, **109**, 183; *A.*, ii, 449.
[5] L. Pauling, *J. Amer. Chem. Soc.*, 1923, **45**, 2777; *A.*, 1924, ii, 110.
[6] E. A. Owen and G. D. Preston, *Proc. Physical Soc.*, 1924, **36**, 341.
[7] O. Hassel and H. Mark, *Z. Physik*, 1924, **23**, 269; *A.*, ii, 382.
[8] A. Ogg, *Phil. Mag.*, 1921, [vi], **42**, 163; R. W. James, *ibid.*, p. 193; L. W. McKeehan, *J. Frankl. Inst.*, 1923, **195**, 59.

while a similar structure has been found for arsenic also.[9] An examination of "single-crystal" wires of tin[10] has confirmed the structure arrived at last year by Mark and Pólányi. "Metallic" selenium and tellurium[11] have been examined by the powder method, and a structure deduced which is similar to that of quartz, *i.e.*, three-fold spirals in a trigonal-hexagonal lattice (Γ_h). For selenium and tellurium, respectively, the side of the basal triangle is 4·34 and 4·44 Å.U. and the ratio c/a 1·14 and 1·33.

One of the most powerful methods of attacking the problem of crystal structure is the rotating-crystal method. For this method, crystals of volume less than a cubic millimetre are ample, and with such crystals at one's disposal the examination of metals and alloys would be greatly facilitated. Unfortunately, the common metals usually crystallise in aggregates of very small crystals, thus excluding the use in most cases of any but the powder method, which is all too inadequate for trustworthy conclusions. Clearly, in ordinary metallic crystallisation the number of centres of crystallisation is so enormous that undercooling is in general impossible. In recent years, several attempts have been made, with varying degrees of success, to overcome this difficulty and grow large single crystals of metals. The products have, of course, provided invaluable aid to crystal analysts, but, furthermore, they have shown that the properties of single metallic crystals are quite different from those of the usual aggregates of microscopic crystals. For instance, zinc crystals have shown themselves to be more plastic even than lead, a stress of only 35 g. per sq. mm. being sufficient to produce permanent deformation, whilst an elongation up to 500% can take place without rupture. Several methods of producing large single metallic crystals have been devised, in which connexion we may mention the work of Tammann, Czockralski, Carpenter and Elam, Bridgeman and others. A rather elegant modification of Tammann's method has just been described by Obreimov and Schubnikov.[12] The metal is melted in a glass tube drawn out to a capillary at the lower end. If the volume of this capillary end is sufficiently small, it will contain a single metal crystal, and from this unique centre crystallisation can be caused, by a careful extension of the cooling from the capillary upwards, to spread throughout the tube without the appearance of other centres of crystallisation, that is, a single

[9] A. J. Bradley, *Phil. Mag.*, 1924, [vi], **47**, 657; *A.*, ii, 382.
[10] A. E. van Arkel, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 97.
[11] M. K. Slattery, *Physical Rev.*, 1923, **21**, 378; *A.*, 1924, ii, 849; A. J. Bradley, *Phil. Mag.*, 1924, [vi], **48**, 477; *A.*, ii, 817.
[12] I. Obreimov and L. Schubnikov, *Z. Physik*, 1924, **25**, 31; *A.*, ii, 721.

metallic crystal of any desired shape (that of the vessel in which the melting takes place) can be grown. To avoid the formation of oxide, the tube must be evacuated; this also removes occluded gas. In this fashion, bismuth, tin, zinc, magnesium, and aluminium were all crystallised without much difficulty. For details regarding certain points, reference should be made to the original paper. It is interesting to note that the maximum cross-section of the capillary, for the formation of a monocrystalline block, varies with the metal.

It seems reasonable to expect that methods of crystallisation similar to the one just described would prove effective in the case of non-metallic substances which resist the usual methods of growing large crystals and yet can be melted without decomposition—such, for instance, are the higher paraffins and fatty acids. One hopes that the scope of this method will be successfully extended to other than metallic systems. And while on the subject of the growth of large crystals, it is convenient to mention here that cubes of rock-salt of side up to 3 cm. have been recently grown from brine containing 0·1% of sulphuric acid and 0·1% of lead nitrate,[13] a striking example of the subtleties of a comparatively little known branch of crystallography.

As mentioned above, the metallic "single-crystals" have proved of great value to *X*-ray analysts. In this connexion should be read a paper on the determination of the crystal-axes in such crystals,[14] one on some of their properties,[15] and two papers on the properties and deformation of fine tungsten wires composed of crystals many of which occupy locally the complete volume of the wire.[16]

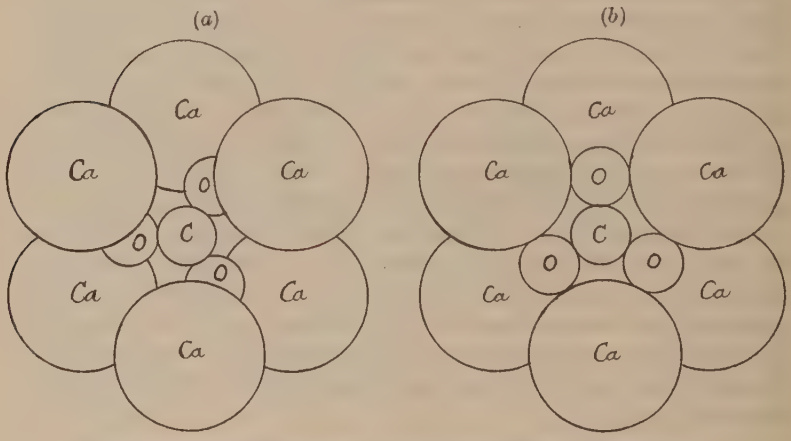
The Structure of Aragonite, etc., and the Calculation of Refractive Indices from Crystal-structure Data.

The beginning of 1924 saw the appearance of a paper[17] by W. L. Bragg on the crystal-structure of aragonite, the orthorhombic form of calcium carbonate. It will be remembered that the rhombohedral form, calcite, was one of the earliest crystals to be elucidated by the method of *X*-rays, and now, after the lapse of several years, the more difficult analysis of the less symmetrical dimorph has, we believe, been successfully accomplished. The lattice is simple orthorhombic (Γ_0), 4·94 × 7·94 × 5·72 Å.U.,

[13] W. E. Gibbs and W. Clayton, *Nature*, 1924, **113**, 492; *A.*, ii, 335.
[14] A. Müller, *Proc. Roy. Soc.*, 1924, [*A*], **105**, 500.
[15] P. W. Bridgeman, *Proc. Nat. Acad. Sci.*, 1924, **10**, 411; *A.*, ii, 818.
[16] A. E. van Arkel, *Physica*, 1923, **3**, 76; *A.*, 1924, ii, 558; F. S. Goucher, *Phil. Mag.*, 1924, [vi], **48**, 800.
[17] W. L. Bragg, *Proc. Roy. Soc.*, 1924, [*A*], **105**, 16; *A.*, ii, 109.

with four molecules of $CaCO_3$ per cell; the symmetry is that of the holohedral space-group O_h^{16}. There is a remarkable resemblance between the dimensions and atomic configurations of the two forms, the (CO_3) groups being almost identical in shape and size. Whereas the arrangement of calcium atoms in calcite approximates to that of cubic close-packing, the corresponding arrangement in aragonite is nearly hexagonal close-packing. Corresponding to the fall in symmetry as we pass from calcite to aragonite, we find that the (CO_3) group has lost its triad axis and possesses now only a plane of symmetry, that is, the original equilateral triangle of oxygen atoms has become slightly distorted to an isosceles triangle. The geometrical consequence of this is that the three oxygen

FIG. 1.



Environment of (CO_3) *group in* (*a*) *calcite, and* (*b*) *aragonite.*

atoms in aragonite are not strictly equivalent, but probably this does not mean anything chemically. We should expect the act of crystallisation to be accompanied by slight distortions from the ideal shape of the "free" molecules. Fig. 1, taken from Bragg's paper, gives a clear idea of the essential difference between the calcite and aragonite arrangement.

In both crystals the (CO_3) groups are found between successive (but oppositely directed) triangles of calcium atoms, but whilst in calcite each oxygen "touches" two calciums, in aragonite three calciums are involved, that is, the change from calcite to aragonite is accompanied by a rotation of the (CO_3) groups through 30° to a rather more symmetrical position with regard to the enclosing calcium atoms. The twinning of aragonite about the (110) planes is simply explained by the above structure.

This investigation has very properly been used as the basis of an attempt to co-ordinate the optical properties of the two minerals by aid of the atomic configurations thus revealed by *X*-rays.[18] The following table summarises the striking connexion (pointed out by Mr. T. V. Barker) between them.

Calcite for D line	$\epsilon = 1{\cdot}486$ (Electric vector $\parallel^1$ to triad axis). $\omega = 1{\cdot}658$ (Electric vector $\perp^r$ to triad axis). Uniaxial (axial angle = 0°).	*Aragonite* (2V = 18° 10′ for D line.)	$\alpha = 1{\cdot}530$ (Electric vector $\parallel^1$ to *c*-axis). $\beta = 1{\cdot}681$ (,, ,, ,, ,, *a*-axis). $\gamma = 1{\cdot}686$ (,, ,, ,, ,, *b*-axis). Acute bisectrix . . . *c*-axis. Optic axial plane (100).

The above refractive-indices indicate that the polarisation for a given field is much greater when the field is parallel to the (CO_3) groups than when it is perpendicular to them. Consequently, since the accepted refractivities of the calcium, carbon, and oxygen atoms show that over 80% of the total refractivity is due to the oxygen atoms alone, the origin of the strong birefringence must be looked for in the peculiar form of the (CO_3) groups. This is just what we should expect from a very simple electrostatic consideration of the effect of an electric field on atomic equilateral triangles such as constitute the (CO_3) groups in these crystals. It is easy to see how a field acting in the plane of the triangles will be more effective in causing polarisation (*i.e.*, a separation of positive and negative charges) than would be a field acting perpendicularly to the triangles. Thus, knowing the relative positions of the atoms in the two cases and the extent to which they become polarised under a given electric field (as deduced from the atomic refractivities of the atoms), the way is made clear to a comparatively straightforward calculation. The author, following this line of argument and making the further assumption that the atom, when polarised, has an external field identical with that of an electric doublet placed at its centre, thus calculated the absolute values of the refractive indices and obtained results which differ from the observed values by only 1 or 2%.

This is a great triumph for crystallography and, we confidently hope, only the beginning of a process which will ultimately lead to the exact quantitative analysis of the optics of any given crystalline structure.

The same author, in collaboration with Prof. S. Chapman, has lately extended his work on the rhombohedral carbonates still further into the realms of interatomic reactions. In a paper

[18] W. L. Bragg, *Proc. Roy. Soc.*, 1924, [*A*], **105**, 370.

read before the Royal Society on November 6th an account was given of a calculation of the rhombohedral angle of these carbonates. As in the case of the refractive indices, the assumptions made were exceedingly simple—merely that the atoms of known "sizes" and positions could be treated as hard spheres acting on each other with forces which vary inversely as the square of the distance—and the results are quite satisfactory. The calculated configuration of minimum electrostatic energy possesses an angle differing from the experimental by 3—4° only, and for the variations of the rhombohedral angle, as we pass along the series, the results are better still.

While on the subject of these rhombohedral carbonates it is convenient to mention here a recent paper by Wyckoff and Merwin [19] in which the authors describe an *X*-ray analysis of the structure of dolomite. They have confirmed what has been long suspected of dolomite,[19a] that it is of lower crystal symmetry than calcite—an observation which alone shows that it is not merely a mixed crystal of approximate molecular proportions but a true chemical compound, $CaCO_3$,(Mg,Fe)CO_3, with a crystal-form of its own. It is noteworthy that the magnesium is replaceable by iron up to 30% with scarcely any change in dimensions, a fact which indicates a striking similarity between these two elements when in this form of combination. The space-group is probably C_{3i}^2 (*i.e.*, rhombohedral symmetry), one molecule of $CaCO_3$,(Mg,Fe)CO_3 per cell, with the following atomic positions: Ca, (000) [or $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$]; Mg (or Fe), $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ [or (000)]; C, (uuu) $(\bar{u}\bar{u}\bar{u})$; O, (xyz) (yzx) (zxy) $(\bar{x}\bar{y}\bar{z})$ $(\bar{y}\bar{z}\bar{x})$ $(\bar{z}\bar{x}\bar{y})$; which means that the structure resembles that of calcite, except that alternate layers (perpendicular to the triad axis) of calcium atoms are replaced by atoms of magnesium (or iron). As before, the (CO_3) groups are enclosed between the successive layers of metallic atoms.

The Structure of Graphite and Related Compounds.

One of the most interesting crystallographic researches of the year, and one which is of direct interest and possibly of great significance for chemists, is the determination of the structure of graphite. Largely owing to the difficulty of obtaining single crystals, convincing work on this substance has been long delayed. It is true that two independent investigations were carried out in 1917,[20] but the powder method used in those researches led to

[19] R. W. G. Wyckoff and H. E. Merwin, *Am. J. Sci.*, 1924, [v], **8**, 447.

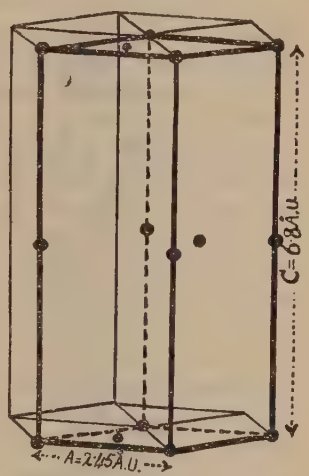
[19a] W. L. Bragg, *Proc. Roy. Soc.*, 1914, [*A*], **89**, 488.

[20] Hull, *Physical Rev.*, 1917, **10**, 661; Debye and Scherrer, *Physikal. Z.*, 1917, **18**, 291.

conflicting results, Hull advocating a hexagonal and Debye and Scherrer a rhombohedral lattice. Since then, Hall's structure has found most favour, perhaps because it is built up of hexagonal rings of carbon atoms, recalling the well-known concept of organic chemistry and a similar arrangement in the structure of diamond. Although the evidence is definitely against Hall's choice of individual atomic positions, this year's work has shown that the preference for his structure was justified to the extent that the hexagonal lattice chosen by him is correct. The structure of Debye and Scherrer must be rejected.

The results of two more investigations (also quite independent) have been published almost simultaneously by Hassel and Mark [21] in Germany and by Bernal [22] in England. It is exceedingly gratifying that the conclusions drawn in the two examinations are identical. In both cases, the chief method of attack was by means of rotation photographs of single crystals of natural and of artificial graphite, but the deductions from these have been strongly confirmed by other results from the ionisation, powder, and Laue methods, respectively. Experimentally, the two researches have followed similar lines, as is natural, but, strangely enough, the theoretical discussions are so dissimilar that we cannot now but believe that their identical conclusions have at last given us the true structure of graphite.

FIG. 2.



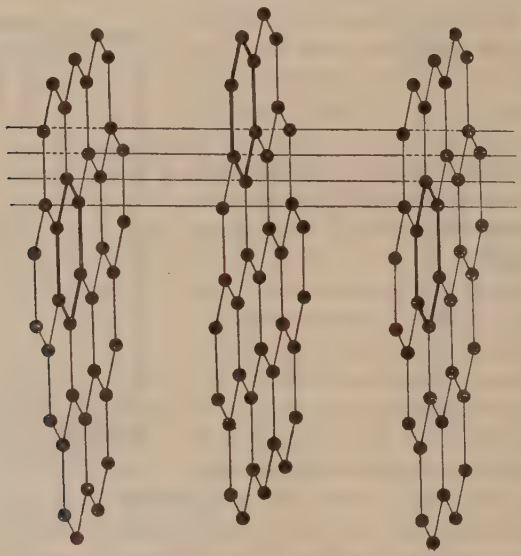
As mentioned above, the unit cell (Fig. 2) is of the hexagonal type and contains four atoms. The dimensions are (*a*) $c = 6{\cdot}79$, $a = 2{\cdot}46$ (Hassel and Mark), (*b*) $c = 6{\cdot}82 \pm 0{\cdot}04$, $a = 2{\cdot}45 \pm 0{\cdot}03$, $c/a = 2{\cdot}77$ (Bernal). Repetition of this cell produces the structure shown in Fig. 3, consisting of layers of *flat* hexagonal rings of carbon atoms separated by a comparatively large distance (3·4 Å.U.). The distance of closest approach of the carbon atoms in the hexagons is about 1·43 Å.U., as opposed to 1·54 Å.U. in diamond. The symmetry of the complete structure is apparently hexagonal holohedral, D^3_{6h}.

The structure of graphite shows remarkable differences from that possessed by diamond, as, indeed, it is right to expect. The

[21] O. Hassel and H. Mark, *Z. Physik*, 1924, **25**, 317; *A.*, ii, 721.
[22] J. D. Bernal, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 749.

great difference in mechanical properties, due to the fact that in the former the atoms are linked closely in one plane only, and the absolutely opposed optical properties, due to the "looseness" of the fourth electron in graphite, are *consequences not merely of different arrangements of similar atoms, but of a fundamental difference in the natures of the atoms themselves.* Whereas it appears reasonable to adopt Bohr's earlier carbon atom (*i.e.*, four 2_1 orbits arranged tetrahedrally) for the diamond, his later suggestion (three 2_1 orbits and one 2_2 orbit) is more suitable to graphite, the unique fourth electron being undoubtedly the cause of the metallic properties which characterise this substance, and of the

FIG. 3.



great difficulty which is experienced on attempting to convert it into diamond.[23]

An interesting confirmation of the uniaxial nature of graphite has recently been carried out by P. Gaubert,[24] who has shown that in very thin flakes graphite is green by transmitted light, and that it is uniaxial, optically negative, and has a refractive index of about 2.

The precise significance of the graphite structure to organic

[23] For a fuller discussion of the part played by the carbon atom in crystals, the reader might consult the lecture "The Carbon Atom in Crystalline Structure," W. H. Bragg, *J. Frankl. Inst.*, 1924, **198**, 615.

[24] P. Gaubert, *Compt. rend.*, 1923, **177**, 1123.

chemistry it is somewhat difficult to estimate with confidence. It gives a certain support to the "flat ring hypothesis," and certainly it is in keeping with what is known of the number and constitutions of the benzene substitution products. On the other hand, there is considerable evidence for the "puckered ring," such as is contained in diamond, for there seems little doubt that naphthalene molecules are only centro-symmetrical in the crystalline state, whilst recent work on crystallised benzene indicates the same symmetry for the benzene molecules. At the same time, it is essential to remember that in a puckered centro-symmetrical ring of carbon atoms, even although in such a ring there are, strictly speaking, three different pairs of similar atoms (*i.e.*, each atom is strictly equivalent only to the one diametrically opposite to it), we cannot as yet be quite sure what exactly is the chemical effect, if any, of the geometrical dissimilarity. In other words, we may not up to the present infer that the small geometrical difference between two neighbouring atoms of the ring will of necessity involve a definite difference in the response of these two neighbouring atoms to the action of chemical reagents. Indeed, it seems more likely that the action of such reagents is in general sufficient to overcome any small geometrical differences in the atoms that are acted upon, the final result being a complete change-over to the configuration demanded by the new product. The geometrical configuration of this new product *may* be the same as that of the ring from which it was produced, but there is no *a priori* reason for assuming it to be so. In fact, it is much more reasonable to assume that the apparently conflicting conclusions which have been deduced from different researches on the symmetry of benzene and its products are only expressions of the fact that the symmetry of the ring is *not* so permanent a quantity that it is retained unaltered through successive chemical or physical changes.

Two attempts have been made this year to determine the crystal-structure of benzene. The first [25] was by the powder method and gave results in fair agreement with those obtained by Broomé last year,[26] but by the unaided powder method it was not possible to determine unequivocally the unit cell and the molecular symmetry. The second attempt, by H. Mark,[27] was by the rotating-crystal method. The results give, provisionally, 6·9, 9·7, and 7·4 Å.U. for the three axes, with four molecules of C_6H_6 per cell and a space-group of either Q_h^{11}, Q_h^{15}, or Q_h^{16} (*i.e.*, rhombic bi-pyramidal). The molecule is stated, although on what grounds is

[25] E. D. Eastman, *J. Amer. Chem. Soc.*, 1924, **46**, 917; *A.*, ii, 448.
[26] B. Broomé, *Physikal. Z.*, 1923, **24**, 124.
[27] H. Mark, *Ber.*, 1924, **57**, 1826.

not quite clear, to be centro-symmetrical. A similar conclusion is drawn for hexachloro- and hexabromo-benzene (monoclinic prismatic, C_{2h}^4, two molecules per cell).

Low-temperature Investigations.

Chiefly on the Continent are now in progress investigations of the crystal-structure of various substances solid only at low temperatures. This is not the place to describe in detail the apparatus and technique of these experiments. The rather meagre results obtained to date on such an easily frozen substance as benzene show only too well the great difficulty attending low-temperature crystal-analyses of any but cubic substances. A preliminary account of the Leiden crystal researches is given in the "Reports and Communications of the Fourth International Congress of Refrigeration," London, June, 1924, and it will be sufficient for our purpose to mention briefly the apparatus there described. Powder photographs are taken in an evacuated Debye camera into which projects a fine capillary which is the end of a Dewar flask containing liquid air. The gas to be solidified is admitted to the camera and condenses only on the outside of the cold hollow capillary. Since the latter is located at the centre of the camera, a powder photograph of the fine cylinder of solid gas can be taken in the usual manner. In the above reports, J. de Smedt and W. H. Keesom describe an examination of solid nitrous oxide. The results agree with a cubic cell of side 5·77 Å.U. With four molecules per cell the density is then 1·52, whilst at the freezing point it is known to be 1·229. The authors consider this to be satisfactory enough and proceed to describe a structure in which the alternate members of the eight small cubes into which the unit can be divided are each occupied by one molecule of nitrous oxide, lying along non-intersecting triad-axes—but the arguments and conclusions do not carry conviction. At the same laboratory photographs have been taken of ice, carbon dioxide, nitrogen, oxygen, and argon also, but the results are not yet to hand, except that solid argon has been announced as cubic. This element has also been examined by F. Simon and C. von Simson,[28] who find that it has the close-packed (face-centred) cubic lattice of side 5·42 Å.U. at 40° Abs. From this structure the "atomic radius" is 1·92 Å.U., whilst the "mean atomic radius" of potassium and chlorine in potassium chloride, where they are supposed to have outer electron shells similar to that of argon, is 1·56 Å.U. This difference is considered by the authors as a variation of "atomic radius" with interatomic forces, and, after the manner of Born,

[28] *Z. Physik*, 1924, **25**, 160; *A.*, ii, 588.

is used as the basis for a rough calculation of the interatomic field. They thus arrive at an attractive force between the atoms which is inversely proportional to the 9th power of the distance, and a repulsive force inversely proportional to the 15th power of the distance.

The same problem has been considered at greater length and by aid of information derived by the methods of the kinetic theory by J. E. Jones.[29] He arrives at the 5th and 15th powers for solid argon, and the same values also for potassium chloride and calcium sulphide, if we assume that the sulphur, chlorine, potassium, and calcium ions have the same structure and therefore the same outer field as argon, with the addition of negative and positive electrostatic charges. Incidentally this author mentions that it can be shown from his treatment that, of the three possible cubic structures, the face-centred has the least potential energy.

Simon and von Simson[30] have also investigated the structure of solid hydrogen chloride. They find two modifications, one of which, stable above 98° Abs., is cubic face-centred with side 5·50 Å.U. With regard to the other form, the results are insufficient to show more than that the symmetry is lower than cubic. The density data indicate that hydrogen chloride contracts 15% on freezing and 2·5% on transition at 98° Abs.

We may conclude this section with a brief reference to quite a remarkable result which has been obtained in the Leiden laboratory—that no difference can be detected in the structure of lead when it suddenly becomes supra-conducting near the absolute zero of temperature. The electric resistance suddenly vanishes, but the structure still remains face-centred cubic. This phenomenon recalls an apparently similar behaviour in iron, which is content with only two types of crystal-structure (body-centred for α-, β-, and δ-iron, face-centred for γ-iron), although four modifications of the element have been known for some time. The importance of these seemingly disappointing results must not be lost sight of in any sound theory of magnetism and supraconductivity.

Other Inorganic Crystals.

Rhombic Sulphur.[31]—The symmetry is holohedral, space-group Q_h^{24}, $a = 10{\cdot}61$, $b = 12{\cdot}87$, $c = 24{\cdot}56$ Å.U., and there are *128 atoms per cell.* The space-group Q_h^{24} of the orthorhombic system is face-centred and exactly analogous to the diamond structure in the cubic system, in which, it will be remembered, alternate members of the eight smaller cubes of the unit cell are also occupied.

[29] *Proc. Roy. Soc.*, 1924, [*A*], **106**, 709. [30] *Loc. cit.*, **21**, p. 168.
[31] H. Mark and E. Wigner, *Z. physikal. Chem.*, 1924, **111**, 398; *A.*, ii, 650.

It follows from this structure of α-sulphur that, in the crystal-lattice, groups of 4, 8, or 16 atoms are associated, *i.e.*, *the crystal-molecule is either* S_4, S_8, *or* S_{16}. The centres of gravity of the groups of sixteen atoms form a rhombic diamond lattice.

Ammonium Zirconium and Ammonium Hafnium Fluorides, $(NH_4)_3ZrF_7$ *and* $(NH_4)_3HfF_7$.[32]—These compounds are simple cubic with sides 9·353 and 9·400 Å.U., respectively; four molecules per cell, space-group O_h^4. Like those for potassium chloroplatinate, in which the octahedral $[PtCl_6]$ ion is surrounded by a further sphere of eight potassium ions, the results for these crystals are in accordance with the Werner theory of co-ordination. We first fix our attention on a certain smaller cube at the middle of the unit cubic cell. Alternate corners of this smaller cube are occupied by $[ZrF_6]$ and fluorine ions. The $[ZrF_6]$ complexes are octahedral, although in the crystal possessing strictly only the symmetry of the calcite class (D_{3d}). The six fluorine atoms are each 1·77 Å.U. from the central zirconium atom and 2·5 Å.U. from each other. They may be considered as the first co-ordination sphere. Next we see arranged round them a second sphere of six (NH_4) groups, also arranged octahedrally, each at a distance of 3·52 Å.U. from the centre of the $[ZrF_6]$ complex and 2·71 Å.U. from the nearest of the six fluorines which form the first sphere. To get an idea of the position of these (NH_4) groups in the unit cell, the reader will find it easy and instructive to sketch out for himself such a diagram as is given in the original paper. They are located six at the face-centres of the small inner cube mentioned above, and the other six distributed along the edges of the larger cube constituting the unit cell. Two will be found in each edge, equidistant from the corners. The (NH_4) groups are naturally grouped in an exactly similar fashion about the fluorine atoms of the second kind which, as mentioned above, occupy alternate corners of the small inner cube. Finally, six of the fluorine atoms of the second sort may be considered to form a third sphere about each zirconium, at a distance of 4·66 Å.U.

The above forms a very striking and beautiful piece of crystal-analysis. It will appeal to the chemist also as an equally elegant study in co-ordination. It should be noticed that in the crystal the zirconium atoms and the fluorine atoms of the second sort have the twelve-fold symmetry of the calcite class, (D_{3d}), the nitrogen atoms have the four-fold symmetry of the rhombic pyramidal class, and the fluorine atoms constituting the $[ZrF_6]$ complexes only the two-fold symmetry of the monoclinic domatic class. From the density of the impure hafnium salt (containing

[32] O. Hassel and H. Mark, *Z. Physik.*, 1924, **27**, 89; *A.*, ii, 817.

15% of the zirconium salt) the atomic weight of hafnium works out to be $179 \pm 5{\cdot}4$.

Calomel.[33]—In the case of this crystal, the tetragonal cell ($6{\cdot}30^2 \times 10{\cdot}90$ Å.U.) contains eight mercury atoms and eight chlorine atoms, which are arranged in a fashion which recalls that of rock-salt, except that in the vertical rows of atoms we have, not ClHgClHg . . . . ., but ClClHgHgClClHgHg . . . . . From Hg to Cl vertically is 2·72 Å.U., while horizontally it is 3·15 Å.U. This result is considered by the author to indicate the formula Hg_2Cl_2.

Aluminium Nitride.[34]—This is a hexagonal close-packed arrangement ($a = 3{\cdot}11$ Å.U. and $c/a = 1{\cdot}60$), in which each atom of either kind is surrounded tetrahedrally by four atoms of the other kind, the interatomic distance being 1·89 Å.U.

Other Organic Crystals.

(a) *Succinic Acid*, (b) *Succinic Anhydride*, (c) *Succinimide.*[35]—(*a*) Monoclinic holohedral (C_{2h}^2) with two molecules per cell. The structure suggested makes the molecule symmetrical about a plane (centro-symmetry is the only alternative) containing both CO_2H groups, and readily explains the cleavage and twinning. (*b*) The crystal class is either rhombic pyramidal (C_{2v}^1), molecules asymmetric, or rhombic bipyramidal (Q_h^1), molecular symmetrical about a plane. (*c*) Symmetry again Q_h^1, molecules asymmetric. A simple structure is suggested which is in conformity with the conclusions drawn for the acid. In both cases, a tetrahedral arrangement of the four carbon atoms is indicated.

(a) *Acetaldehyde-ammonia*, (b) *Metacetaldehyde.*[36]—(*a*) Is ditrigonal scalenohedral (D_{3d}^5) with six molecules per cell. These can be so arranged in the cell, each molecule being symmetrical about a plane, that the aldehyde groups of the separate chemical molecules are adjacent. This is taken by the authors to indicate a tendency to polymerisation even in the crystalline state; (*b*) is tetragonal, either C_4^5 or C_{4v}^9. The cell is body-centred and contains eight acetaldehyde molecules, not more than four of which can form a crystal-molecule. The polymeride cannot be thus more complex than tetrameric.

Oxalic Acid.[37]—The anhydrous acid is rhombic bipyramidal, space-group Q_h^{15} with four molecules per cell. The molecules are centro-symmetrical and show no obvious association with each other. The dihydrate is monoclinic prismatic, space-group C_{2h}^5,

[33] C. Mauguin, *Compt. rend.*, 1924, **178**, 1913; *A.*, ii, 588.
[34] H. Ott, *Z. Physik*, 1924, **22**, 201; *A.*, ii, 298.
[35] K. Yardley, *Proc. Roy. Soc.*, 1924, [*A*], **105**, 451; *A.*, ii, 382.
[36] O. Hassel and H. Mark, *Z. physikal. Chem.*, 1924, **111**, 357; *A.*, ii, 651.
[37] H. Hoffmann and H. Mark, *Z. physikal. Chem.*, 1924, **111**, 321; *A.*, ii, 650.

two molecules per cell. These are again centro-symmetrical, the water being apparently part of the molecule.

(a) *Carbon Tetraiodide*, (b) *Carbon Tetrabromide*.[37]—In the cubic form both (*a*) and (*b*) appear to have the simple cubic lattice, and, if the crystallographic evidence can be taken to indicate the hexakis tetrahedral class (T_d^1), each molecule is then tetrahedral; (*b*) in the monoclinic prismatic form possesses eight molecules of CBr_4 per cell, space-group either C_{2h}^3 or C_{2h}^6. The author concludes that the crystal-molecule is C_2Br_8, which accounts for the change from cubic to monoclinic, since the two CBr_4 molecules distort each other.

Miscellaneous.

Piezo-electricity and Molecular Dissymmetry.[38]—In this study use has been made of amplification by valves. More than thirty optically active substances, including camphor derivatives, alkaloids, and complex salts, have been tested and found to be piezo-electric. In many of these structures the absence of a centre of symmetry would not have been deduced from the habit or corrosion figures. The author thus recommends this method as very reliable when ordinary methods fail.

Rotatory Dispersion of Tartaric Acid.[39]—Longchambon finds that in the crystalline state the rotatory dispersion of tartaric acid is strong but quite normal. The ratio for the rotations of the indigo and yellow mercury lines is 2·14. From examination of the dispersion of solutions he concludes that the dispersion of the lævo-component contributing to the anomalous dispersion of the solutions is between 2 and 2·2, a fact which is then taken to prove the identity of this lævo-component with the active system present in the ordinary crystallised acid.

Deformation and Strength of Crystals.[40]—The "elastic-limit" of a crystal, as defined by the minimum strain producing distortion of the Laue photograph, is a well-defined constant for a given material and temperature. It decreases to zero at the melting point. With rock-salt, beyond this elastic limit, gliding takes place along the (110) planes, the spots belonging to these planes alone remaining sharp on the Laue photograph. The plastic deformation increases its tensile strength some twelve times. The theoretical and observed values of the tensile strength of rock-salt do not agree, but this is probably explained by surface cracking, which is healed by immersion in water. Crystals immersed in water have a greatly increased tensile strength.

[38] R. Lucas, *Compt. rend.*, 1924, **178**, 1890; *A.*, ii, 586.

[39] L. Longchambon, *ibid.*, p. 951; *A.*, ii, 373.

[40] A. Joffé, M. Kirpitschewa, and M. A. Lewitzky, *Z. Physik*, 1924, **22**, 286.

New Books.

(1) "The Natural History of Crystals." By Dr. A. E. H. Tutton. Pp. xii + 287 + 33 plates. (London: Kegan Paul and Co., Ltd., 1924.) 15*s*. net.—This is a charming, semi-popular book in Dr. Tutton's inimitable style. It has been brought very much up to date (it is really a re-issue of his well-known book "Crystals," published in 1911) and forms a fascinating story from beginning to end. It is beautifully illustrated.

(2) "Elementary Crystallography." By Dr. J. W. Evans and G. M. Davies. Pp. vii + 134. (London: Thomas Marby & Co., 1924.) 9*s*. 6*d*. net.—This book is intended as a concise but easy introduction to crystallography, and is admirable except in so far as it advocates still another nomenclature for use when describing the thirty-two crystal classes. At the present stage of the subject, when its rapidly growing importance necessitates avoiding anything which might impede its assimilation by students of other branches of science, such an attempt to introduce still another notation is not well advised.

(3) "La Structure des Cristaux." By Ch. Manguin. Pp. 281 + 125 figures. Vol. 6 des Conférences-Rapports de Documentation sur la Physique. (Paris: Libraire Scientifique Albert Blanchard, 1924.) 20 Francs.—For any one who is in need of a thorough, but not too abstruse or expensive, work on the methods and results of crystal-analysis, we can heartily recommend this book by the well-known French crystallographer. The last part of the book is devoted to a survey of the various types of crystal-structure as revealed by *X*-ray analysis and structure-theory, and there is also a very good bibliography

(4) "The Structure of Crystals." By Ralph W. G. Wyckoff. A. C. S. Monograph No. 19. Pp. 464 + 213 illustrations. (New York: The Chemical Catalogue Company, Inc., 1924.) $6·00.—This is no doubt the most complete text-book on crystal-analysis that has yet been written, and is deserving of the highest praise for the enormous amount of labour which it must have involved. Although written for the American Chemical Society, it is probably too difficult for those who have not had a fairly thorough grounding in crystallography—but as a book of reference for crystal-analysts it is unique. The latter part of the book includes a complete survey of known crystal-structures and an exhaustive bibliography carried up to the end of 1923. It is unfortunate that still another notation is recommended. Whatever the short-comings of the Schoenflies system, crystallographers throughout the world have become accustomed to it.

W. T. Astbury.
W. H. Bragg.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.*

The Isotopic Constitution of the Elements.

During the two years covered by this Report steady progress has been made by means of the mass-spectrograph. The discovery of further small deviations from the whole-number rule has necessitated the introduction of the term "mass-number." This is theoretically the number of protons in the atom, practically it is the nearest whole number to its weight expressed on the ordinary chemical scale. These integers are identical in all cases so far as our knowledge extends at present.[1] An investigation of methods by which the positive rays, or as they may now be more generally termed mass rays, of the metallic elements could be generated resulted in the working out of the method of "accelerated anode rays"[2] which has been exceedingly valuable in extending the work to elements with which it is impossible to deal by ordinary gaseous discharge. The first use to which this was put was a verification of the whole-number rule for the light metallic elements. The only one of these to show measurable deviation was lithium. The masses of its isotopes were estimated to be $7{\cdot}006 \pm 0{\cdot}005$ and $6{\cdot}008 \pm 0{\cdot}005$, respectively. No deviation was detected in beryllium, sodium, magnesium, aluminium, potassium, or calcium. This leads to the remarkable conclusion that the two isobaric atoms A^{40} and Ca^{40} probably do not differ in weight by 0·1%, although the structure of their respective nuclei *must* be different, for one contains two more electrons than the other.

Silicon.—The third isotope Si^{30} of this element has been confirmed.[3] Its line is a little less intense than that of Si^{29}, in agreement with the results obtained with band spectra (p. 244).

Scandium, Titanium.[2]—The principal constituents of these two elements, which are probably simple, have mass-numbers 45 and 48, respectively, but the lines were not obtained with sufficient intensity to preclude the possibility of small quantities of isotopes.

Vanadium, Chromium, Manganese, Cobalt.[2]—All these elements gave satisfactory single lines, showing that they are simple and

* This Report covers the years 1923 and 1924.

[1] F. W. Aston, *Phil. Mag.*, 1923, [vi], **45**, 945; *A.*, 1923, ii, 353.

[2] *Idem, ibid.*, 1924, [vi], **47**, 387; *A.*, ii, 225.

[3] *Idem, Nature*, 1924, **114**, 273.

that their mass-numbers correspond to their chemical atomic weights.

Iron.[4]—The second isotope, Fe^{54}, is confirmed. It appears to be present to the extent of about 5%.

Copper.[2]—The effects obtained with copper were faint but very conclusive, as both in intensity and position its lines appeared exactly as statistical considerations had led one to expect. These lines correspond to 63 and 65 and show no measurable deviation from the whole-number rule.

Gallium [2] is also an element consisting of two isotopes. They are of mass numbers 69 and 71. The former is in greater abundance in agreement with the latest value of the atomic weight.

Germanium [2] is a complex element with three isotopes of mass-numbers 70, 72, 74 of intensities roughly proportional to 2 : 4 : 5. As no deviation from whole number is detectable, this suggests a mean atomic weight of 72·6, a value which has been obtained in the recent work of Baxter.[5] It will be noticed that Ge^{70} is isobaric with the weakest and heaviest isotope of zinc and that Ge^{74} is isobaric with the very weak, lightest isotope of selenium.

Strontium.—In the first analysis of this element [2] it appeared to consist entirely of atoms of mass-number 88, but later results [4] revealed a very faint companion at 86. The principal line gives evidence of divergence from a whole number, its mass being estimated as 78·8. Even with this allowance, the present chemical atomic weight is probably a little low.

Yttrium [2] is a simple element of mass-number 89.

Zirconium.—The analysis of this element has presented peculia difficulties.[6] It gives mass lines 90, 92, 94 and a doubtful one (96). The masses appear to be a little less than whole numbers.

Silver [2] gives results exactly in accordance with expectation, having two isotopes, 107, 109, almost equal in intensity.

Cadmium is a very complex element.[7] It has six isotopes, 110, 111, 112, 113, 114, 116, and their order of intensity appears identical with that of the first six isotopes of tin. This is a very striking coincidence, and may have a deep significance in connexion with the relative stability of the nuclei of isotopes.

Indium [8] appears to be simple 115, but the line is not sufficiently intense to preclude the possibility of other constituents in small proportion.

[4] F. W. Aston, *Nature*, 1924, **113**, 856; *A.*, ii, 445.

[5] G. M. Baxter and W. C. Cooper, jun., *Proc. Amer. Acad. Arts Sci.*, 1924, **59**, 235; *A.*, ii, 690.

[6] F. W. Aston, *Nature*, 1924, **114**, 273; *A.*, ii, 649.

[7] *Idem, ibid.*, 717.

[8] *Idem, ibid.*, 192.

Table of Elements and Isotopes.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Mass-numbers of isotopes in order of intensity.
H	1	1·008	1	1
He	2	4·00	1	4
Li	3	6·94	2	7, 6
Be	4	9·02	1	9
B	5	10·82	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22
Na	11	23·00	1	23
Mg	12	24·32	3	24, 25, 26
Al	13	26·96	1	27
Si	14	28·06	3	28, 29, 30
P	15	31·02	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37
A	18	39·88	2	40, 36
K	19	39·10	2	39, 41
Ca	20	40·07	2	40, 44
Sc	21	45·10	1	45
Ti	22	48·10	1	48
V	23	51·00	1	51
Cr	24	52·00	1	52
Mn	25	54·93	1	55
Fe	26	55·84	2	56, 54
Co	27	58·97	1	59
Ni	28	58·68	2	58, 60
Cu	29	63·57	2	63, 65
Zn	30	65·38	4	64, 66, 68, 70
Ga	31	69·72	2	69, 71
Ge	32	72·38	3	74, 72, 70
As	33	74·96	1	75
Se	34	79·20	6	80, 78, 76, 82, 77, 74
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
Rb	37	85·44	2	85, 87
Sr	38	87·63	2	88, 86
Y	39	88·90	1	89
Zr	40	(91)	(4)	90, 94, 92, (96)
Ag	47	107·88	2	107, 109
Cd	48	112·41	6	114, 112, 110, 113, 111, 116
In	49	114·80	1	115
Sn	50	118·70	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121·77	2	121, 123
Te	52	127·5	3	128, 130, 126
I	53	126·92	1	127
X	54	130·20	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132·81	1	133
Ba	56	137·37	(2)	138, (136)
La	57	138·91	1	139
Ce	58	140·25	2	140, 142
Pr	59	140·92	1	141
Nd	60	144·27	(4)	142, 144, 146, (145)
Hg	80	200·60	(6)	(197), 202, 204, 198, 199, 200
Bi	83	209·00	1	209

(Numbers in brackets are provisional only.)

Tellurium.—This element, which has a special interest in connexion with its anomalous position in the table of atomic weights, gives three lines, 126, 128, 130, of intensity roughly 1 : 2 : 2. Although these appear to be due to masses rather less than whole numbers, the mean weight seems probably more than 128.[7] The chemical one at present in use is 127·5, but a new method of determination gives 127·8.[8a] Tellurium appears to have all its mass-numbers shared by xenon.

Barium was at first thought to be a simple element of mass-number 138 with an actual atomic mass of about 137·8.[9] A second search under more advantageous conditions indicated possibilities of a very faint companion 136.[6] This is, however, quite inadequate to account for the chemical atomic weight 137·37, which is probably too low.

Lanthanum, *Praseodymium* are both simple elements of mass-numbers 139 and 141, respectively, as their chemical atomic weights would lead one to expect.[9]

Cerium has a strong isotope 140 and a weak one 142.[6]

Neodymium is complex with mass-numbers 142—isobaric with cerium—144, 146 and possibly (145).[6]

Bismuth.[7]—This is the heaviest element which has been analysed so far. It gives a single line and is doubtless a simple element of mass-number 209, as its atomic weight suggests.

In addition to these results, Dempster has confirmed his previous conclusions on calcium and zinc.[10] It will be seen from the table of isotopes given that, with the exception of a gap of five, Nb—Pd, all the known elements up to atomic number 60 have been analysed.

The Periodic System of the Elements.

Certain arithmetical regularities connecting atomic number with atomic weight and valency have been pointed out by F. Loewinson-Lessing [11] and by A. Ríus y Miró.[12] Harkins has further developed his system of atomic species with particular relation to their nuclear stability and isotopic number.[13] The most important contribution to this branch of the subject is that of A. S. Russell,[14] who, in a series of papers, has applied the known properties of radioactive bodies to predict the occurrence and relative abundance of the

[8a] P. Bruylants and J. Michielsen, *Bull. Acad. roy. Belg.*, 1919, **5**, 119; *A.*, 1923, ii, 153.

[9] F. W. Aston, *Nature*, 1924, **113**, 857.

[10] A. J. Dempster, *Physical Rev.*, 1922, **20**, 631; *A.*, 1923, ii, 413.

[11] *Compt. rend.*, 1923, **176**, 307; *A.*, 1923, ii, 146.

[12] *Anal. Fis. Quím.*, 1922, **20**, 496; *A.*, 1923, ii, 146.

[13] *J. Amer. Chem. Soc.*, 1923, **45**, 1426; *A.*, 1923, ii, 553.

[14] *Phil. Mag.*, 1924, [vi], **47**, 1121; **48**, 365; *A.*, ii, 445.

isotopes of the inactive elements. He does not assume, nor is it essential to his theory, that all elements are actually evolved by radioactive disintegration. His method is to arrange all known and hypothetical radioactive elements and their products into four series, two real and two hypothetical, and examine the periodic behaviour as regards stability. The relations so found he then applies to the elements generally. A study of this periodic behaviour leads, for instance, to three fundamental rules: (*a*) The maximum difference in mass-number of any group of isotopes is 8. (*b*) Elements of odd atomic number may have two odd mass-numbers only, and these differ by two units. (*c*) Elements of even atomic number may have both odd and even mass-numbers, and (with two exceptions) the number of the former is limited to two and their difference is two units. These are not seriously contravened by the known isotopes of the elements of fairly high atomic number to which he confines his general argument. From these and several other relations derived in the same way together with a few reasonable assumptions, he is able to predict the isotopes of an element from its atomic weight. Although his arguments are in some cases difficult to follow and to appraise, the success of his predictions is certainly noteworthy. We have here one of the first definite steps towards the enunciation of a periodic law which we shall be able to apply to the nuclear properties of atoms just as the present one can be applied to their extranuclear or chemical ones.

Abundance of Atomic Species.—Some interesting deductions on the stability of nuclei have been obtained by plotting on a logarithmic scale the abundance of each known atomic species against its mass-number.[15] This clearly shows the extreme discrepancy between the ratio of the abundance of the isotopes of a single element and the ratio of the abundance of the elements themselves, *e.g.*, there are only about three Cl^{35} atoms to one Cl^{37} and about two Ga^{69} atoms to one Ga^{71}, yet there are 10^9 times more atoms of chlorine than of gallium. In the case of elements of odd atomic number, it is shown to be impossible to ascribe this to the limited range of methods of detection of isotopes. Hence it must be concluded that isotopes of an element have some nuclear property in common in addition to that of identical nuclear charge. This conclusion is supported by the relative masses of the isotopes of tin and xenon and also by other general considerations of nuclear structure. Furthermore,[16] the abundance on the earth of the inert gases appears to be about 10^6 times less than that expected from

[15] F. W. Aston, *Nature*, 1924, **113**, 393.
[16] *Idem*, *ibid.*, **114**, 786.

the form of the curve for other elements. It is suggested that the loss of the inert gases from the earth may have taken place during the evolution of the solar system.

Constancy of Chemical Atomic Weight.

Several attempts have been made to detect differences of atomic weight between samples of a complex element from different sources due to variation in the proportional abundance of its constituent isotopes. The results, as before, are strongly negative. The claim [17] to have detected differences in the atomic weight of antimony from various sources carries no weight, for the determinations are provisional only and have not been confirmed. The low combining weight of lead in a Vesuvian contunnite is naturally attributed to the presence of uranium lead.[18] Baxter [19] has repeated his previous comparison between meteoric and terrestrial nickel and finds an identical atomic weight, 58·70, for both. He has also examined cobalt of meteoric and terrestrial origin, and both varieties give the same value, 58·94.[20] A most important and conclusive paper on the subject is that of F. M. Jaeger and D. W. Dijkstra.[21] After a general discussion of the evidence already available, they go on to describe their own experiments. In these, they worked on the element silicon, which has as wide a distribution in nature as any complex element, and examined it by determining the density of tetraethylsilicane made from it by the Grignard reaction. After carrying out this operation with silicons from six different cosmic and six different terrestrial sources, they found no differences of density greater than 0·0006%. By further investigation they were able to show conclusively that even these small differences are to be attributed to the presence of traces of by-products too small to be detected chemically. They conclude that terrestrial and meteoric silicon give products of density not differing by more than the error of experiment, that is 0·00004%, so that the ratio of the isotopes of silicon is constant within the limits of the highest accuracy attainable at present. It is clear from such results as these that, although the figure for the chemical atomic weight of a complex element, depending as it does on the proportion of its isotopes, may not be so fundamental

[17] Sheikh D. Muzaffar, *J. Amer. Chem. Soc.*, 1923, **45**, 2009; *A.*, 1923 ii, 771.

[18] A. Piutti and D. Migliacci, *Atti R. Accad. Lincei*, 1923, **32**, 468; *A.*, ii, 181.

[19] G. P. Baxter and F. A. Hilton, *J. Amer. Chem. Soc.*, 1923, **45**, 694; *A.*, 1923, ii, 326.

[20] G. P. Baxter and M. J. Dorcas, *ibid.*, 1924, **46**, 357; *A.*, ii, 341.

[21] *Proc. K. Akad. Wetensch Amsterdam*, **27**, Nos. 5 and 6.

as its atomic number or the mass-numbers and actual masses of its constituent atoms, yet it may for normal inactive elements be treated as a true constant of nature, since no process in nature seems capable of changing it.

The Spectra of Isotopes.

In connexion with series spectra, there is comparatively little to report. A. L. Narayan [22] has subjected the tin lines 5631 and 4524 to the highest resolution by means of a Lummer plate. Even when the pressure was of the order of 1 mm., both lines were simple in structure, the latter being especially sharp. Since tin is a complex element with isotopes ranging from 116 to 124, this result contradicts McLennan's view [23] that the spectral displacement for isotopes should be given by the atomic number multiplied by the displacement calculated on Bohr's theory. H. Nagaoka and his collaborators [24] have investigated the satellites of mercury and bismuth lines and have formulated a theory that these are caused by isotopes. There is little to recommend this view and it has been unfavourably criticised by G. Runge [25] and by R. S. Mulliken.[26] This view has led its authors to predict seven isotopes of bismuth, an element since shown to be simple.

Band Spectra.—Mulliken has made a very noteworthy advance in this field.[27] He shows that the band spectrum attributed by Jevons to boron nitride is probably due to boron oxide and really consists of two superposed spectra. These are related to each other exactly as would be predicted by the quantum theory of band spectra if the more intense spectrum is due to the more abundant isotope, $B^{11}O$, and the less intense band to the less abundant isotope, $B^{10}O$. This result furnishes strong support for the main features of the theory and leaves no doubt as to the isotopic nature of the two related band spectra. In agreement with the results of the mass-spectrograph, there is no evidence of the existence of more than two isotopes of boron. With silicon nitride, photographs show that each sufficiently intense $Si^{28}N$ head of bands on the red side of the central band of the system is accompanied by two very much weaker heads, one at double the distance of the other. These correspond with isotopes Si^{29} and Si^{30}; the former appears to be a little more abundant than the

[22] *Nature*, 1923, **112**, 651; *A.*, 1923, ii, 807.
[23] *A.*, 1922, ii, 541, 728.
[24] *Nature*, 1924, **113**, 459, 532; **114**, 245; *A.*, ii. 295, 649.
[25] *Ibid.*, **113**, 781; *A.*, ii, 446.
[26] *Ibid.*, **113**, 820; *A.*, ii, 446.
[27] *Science*, 1923, **58**, 164; *A.*, ii, 3; *Nature*, 1924, **113**, 423, 489; *A.*, ii, 294, 295.

latter, and there is no evidence of any other isotope. Results of a similar nature are given by hydrides, but here the separation is much smaller on account of the great difference between the masses of the atoms combining.

The Separation of Isotopes.

Work in this field shows a considerable diminution on that done during 1921—1922. This was to be expected, since most of the obvious methods have been exhaustively tested and few new ones have been devised. Further experiments have been done on their evaporation method by Brönsted and Hevesy, who have attempted to separate the isotopes of which ordinary lead is supposed to consist by the vacuum distillation of lead chloride. The final fractions were submitted to Hönigschmid [28] for atomic weight determination. The mean result for the more volatile fraction was $207{\cdot}229 \pm 0{\cdot}003$ and for the less volatile $207{\cdot}236 \pm 0{\cdot}003$, a difference too small to warrant any claim for separation. Harkins [29] describes a large steel apparatus in which 2·5 kg. of mercury can be dealt with in one operation. The use of liquid air is avoided and cooling is carried out with ice and in such a way that the fractions can be drawn off continuously. After 268 hours of operation with this apparatus and 37 hours with a smaller glass one, they obtained a light fraction of 3·8 g. of mercury, showing a decrease in atomic weight of 0·044 of a unit, and a heavy fraction of 4·4 g., showing an increase of 0·052 of a unit. G. Hertz [30] has investigated the rates of gaseous diffusion against a moving column of water vapour, and has designed an admirable apparatus for the continual separation of helium from neon on a commercial scale. He suggests that the method should give a large separation of the isotopes of neon if the apparatus was suitably modified, but no success has been reported so far. The possibility of separation of isotopes by ionic migration has been examined by several observers. This was first suggested by Lindemann, but gave negative results.[31] In the experiments of Kendall [32] the conditions were so arranged that the ions moved in an agar-agar gel at the rate of 12 to 18 inches a day. With this arrangement, quantitative separation of sodium iodide from sodium thiocyanate was obtained after a

[28] O. Hönigschmid and M. Steinheil, *Ber.*, 1923, **56**, [*B*], 1831; *A.*, 1923, ii, 764.

[29] W. D. Harkins and S. L. Madorsky, *J. Amer. Chem. Soc.*, 1923, **45**, 591; *A.*, 1923, ii, 322.

[30] *Z. Physik*, 1923, **19**, 35.

[31] J. G. Pilley, *Nature*, 1923, **111**, 848; *A.*, 1923, ii, 554.

[32] J. Kendall and E. D. Crittenden, *Proc. Nat. Acad. Sci.*, 1923, **9**, 75; *A.*, 1923, ii, 282.

movement of only a few feet, but there was no indication of any separation in the case of sodium chloride even after a movement of 100 feet. E. Murmann [33] has described many attempts to separate isotopes by this and other methods. All gave negative results and he concludes that ionic mobilities are dependent only on atomic volume and not on atomic weight. B. L. Vanzetti [34] has tried parchment paper and animal membrane diaphragms to separate the isotopic sodium chlorides. In a later report,[35] he records a slight change in atomic weight. Attempts have also been made to separate the isotopes of chlorine by adsorption on charcoal,[36] but without success. The conclusion given in the last report on this subject,[37] that there was little hope of separating isotopes on anything like a chemical scale, is clearly still justified.

Artificial Disintegration and Transmutation.

Aided by technical improvements in the means of detecting and counting scintillations, Sir E. Rutherford and J. Chadwick [38] have made great advances in their experiments on the disintegration of the nuclei of the lighter elements by bombardment with swift α-particles. By observing from an angle of 90° to the direction of the incident beam, they are able to detect disintegration products down to a range of 7 cm., instead of 30 cm. as previously, and at the same time eliminate all effects from hydrogen contamination in the element bombarded. Working in this way, in addition to the elements boron, nitrogen, fluorine, sodium, aluminium, and phosphorus which give protons of range 40 to 90 cm., they have now detected protons of range above 7 cm. resulting from the disintegration of neon, magnesium, silicon, sulphur, chlorine, argon, and potassium. The numbers of these protons are small, one-third to one-twentieth of the number obtained from aluminium under similar conditions. Their ranges have not yet been measured accurately, but those from neon have the shortest—about 16 cm. The effect with beryllium is small and doubtful. The other light elements, hydrogen, helium, lithium, carbon, and oxygen, give no detectable effect at all. In addition, experiments have been made, but no effects observed, with nickel, cobalt, zinc, selenium, krypton, molybdenum, palladium, silver, tin, xenon, gold, and uranium. A noteworthy point in connexion with this work is the marked

[33] *Oesterr. Chem. Ztg.*, 1923, **26**, 14; *A.*, 1923, ii, 401.
[34] *Gazzetta*, 1924, **54**, 89; *A.*, ii, 404.
[35] *Chem. Zentr.*, 1924, I, 1013; *A.*, ii, 650.
[36] J. Sameshima, K. Aihara, and T. Shirai, *J. Chem. Soc. Japan*, 1922, **43**, 761.
[37] *Ann. Report*, 1922, **19**, 278.
[38] *Nature*, 1924, **113**, 457; *A.*, ii, 296; *Proc. Physical Soc.*, 1924, **36**, 417.

difference in numbers and in range of the dislodged protons between elements of even and those of odd atomic number. This difference is reflected throughout the whole list of elements, not only in their relative abundance in nature, but also in their isotopic constitution, and is doubtless a fundamental one in connexion with nuclear structure and stability.

G. Kirsch and H. Pettersson,[39] working at the Radium Institute, Vienna, have published results on disintegration by α-particles widely different from those summarised above. Using Rutherford's original method, they claim to have disintegrated carbon and oxygen and also to have obtained large effects from beryllium. Time will show if these claims can be substantiated, but in the meanwhile, when it is remembered that the technique of the scintillation method is one full of pitfalls only to be avoided by years of research, the balance of the evidence is overwhelmingly on the side of the more experienced investigators.

A wonderful verification of Rutherford's original discovery of the disintegration of the nitrogen atom by the impact of a swift α-particle has been obtained quite recently in the Cavendish Laboratory by P. M. S. Blackett,[40] who has taken actual photographs, by the Wilson fog-track method, of no fewer than seven of these occurrences. To get these, it was necessary to photograph more than 400,000 α-ray tracks, the probability working out about the same as that estimated by Rutherford. A large number of close nuclear encounters, indicated by widely forked tracks, were picked out and measured. Of these, eight only disobeyed the ordinary collision laws and were undoubtedly due to actual disintegrations. In all these the track of the swift proton dislodged is present both in form and quality exactly as expected, but, contrary to most expectations, there are only *two* branches to the fork. This shows that the colliding α-particle does not rebound along a separate track, but, after impact, is retained by the disintegrating nucleus, at least for the rest of its passage through the gas of the expansion chamber. The nitrogen nucleus will have lost a charge + 1 and a mass 1 and will have gained a charge + 2 and a mass 4, so that the substance formed would appear to be an isotope of oxygen of mass 17. There is no evidence of such a substance, so that it is either unstable or produced in nature in quantities too small to be detected. Previous to Blackett's experiments, Harkins [41] published a Wilson track photograph showing

[39] *Nature*, 1924, **113**, 603; *A.*, ii, 380.

[40] *Proc. Roy. Soc.*, 1925, [*A*], **107**, 349.

[41] W. D. Harkins and R. W. Ryan, *Nature*, 1923, **112**, 54; *A.*, 1923, ii, 601; *J. Amer. Chem. Soc.*, 1923, **45**, 2095; *A.*, 1923, ii, 720.

a fork with *three* branches which he claimed must therefore be that of a disintegration. This claim was doubtful from the first, since the fork occurred too near the end of the range of the α-particle for its energy to be adequate to effect disintegration. The track bears no resemblance to those obtained by Blackett and is most probably due to the effect of radioactive contamination accidentally superposed on an ordinary forked collision track.

A. Piutti [42] has made numerous experiments to find if any formation of helium or neon takes place in the discharge through hydrogen. No trace of either was found. S. K. Allison and W. D. Harkins [43] have repeated the experiments of Wendt and Irion [44] with the greatest care. Tungsten and platinum wires were repeatedly exploded by discharges from a powerful condenser of 0·5 of a microfarad capacity charged to 42,000 volts. A condenser discharge of potential 84,000 volts was passed hundreds of times through mercury vapour at 0·1 mm. pressure and also through hydrogen at 40 mm. pressure. No trace of helium was found in any of these experiments, although a method capable of detecting 2×10^{-10} g. was employed.

The sensational report [45] that mercury had been transmuted into gold in an ordinary mercury vapour lamp still lacks confirmation. It has, however, been supported [46] on the ground that the transmutation only requires the addition of one electron to the mercury nucleus, and since the field near the positively charged nucleus would be one of attraction, not of repulsion, as in the case of an approaching α-particle, this operation might require very little energy. Against this view it may be argued, unless our present ideas of matter are fundamentally at fault, that Nature has provided a mechanism, admittedly unknown to us but certainly extremely difficult to evade, which effectually prevents positively charged nuclei absorbing casual electrons driven in their direction. Otherwise matter could not exist at all. The experiments of Rutherford leave no doubt that just as the dimensions of the nucleus of an atom are almost inconceivably small—the radius of that of aluminium is probably less than 4×10^{-13} cm.—so the forces binding together its component parts are gigantic and to be measured in millions of volts. Until the progress of electrical engineering makes such potentials technically available in the laboratory, it seems unlikely that transmutation of elements on a chemical, as opposed to the radioactive, scale will be possible.

[42] *Z. Elektrochem.*, 1922, **28**, 452; *A.*, 1923, ii, 20.
[43] *J. Amer. Chem. Soc.*, 1924, **46**, 814; *A.*, ii, 407.
[44] *Ann. Report*, 1922, **19**, 280.
[45] A. Miethe, *Naturwiss.*, July 18, 1924.
[46] F. Soddy, *Nature*, 1924, **114**, 244; *A.*, ii, 684.

Long-range Particles from Radioactive Sources.

The emission of particles of abnormal range was first observed in the case of radium-*C* by Rutherford in 1919. A similar phenomenon was found to be exhibited by thorium-*C*.[47] This work has been repeated, and extended to actinium and polonium active deposits by L. F. Bates and J. S. Rogers,[48] using a scintillation method. Their results may be tabulated as follows; the ranges are calculated for air under standard conditions and the numbers of the long-range particles are calculated relative to the total number of normal α-particles emitted.

Radium-*B* -*C*	Range	6·97	9·3	11·1	13·2
	Number	10^7	380	126	67
Thorium-*C*	Range	8·6	11·5	15·0	18·4
	Number	10^6	220	47	55
Polonium	Range	3·93	6·1	10·0	13·1
	Number	10^7	91	51	26

In addition, actinium deposit was found to emit particles of range 6·49 cm., previously recorded by E. Marsden and P. B. Perkins,[49] to the extent of 0·322% of its total α-rays. The work of Bates and Rogers on radium active deposit was adversely criticised by G. Kirsch and H. Pettersson,[50] who state that no particles are emitted from this substance of range greater than 7·5 cm. In consequence of its importance in connexion with their work on disintegration, Rutherford and Chadwick [51] have reviewed the case of radium active deposit and reinvestigated it exhaustively by a great variety of experiments intended to eliminate any possible flaws in the evidence. They have varied the preparation of the source, examined the particles in a great variety of gases, eliminated the possibility of holes in the screens by replacing these with a heavy gas such as xenon, and finally have determined the mass and velocity of the particles themselves by direct measurement of their deflection in a magnetic field. From the evidence so obtained, they conclude definitely that the long-range particles are α-particles of mass 4 and that their origin is in the source itself and not in the surrounding material. They estimate the number of long-range particles emitted by 1 mg. of radium-*C* as about 1050 of range 9·3 cm. and 180 of range 11·2 cm., numbers corresponding to 309 and 53, respectively, on the scale of Bates and

[47] *Ann. Report*, 1922, **19**, 286.
[48] *Nature*, 1923, **112**, 435; *A.*, 1923, ii, 720; *Proc. Roy. Soc.*, 1924, [*A*], **105**, 97, 360; *A.*, ii, 84, 296.
[49] *A.*, 1914, ii, 410.
[50] *Nature*, 1923, **112**, 687; 1924, **113**, 641; *A.*, 1923, ii, 819; 1924, ii, 380.
[51] *Phil. Mag.*, 1924, [vi], **38**, 509.

Rogers given above. They do not find any evidence of the particles of range 13·2 claimed by Bates and Rogers.

Radiations and the Structure of the Nucleus.

S. Rosseland [52] suggests that the nuclei of radioactive elements may be intrinsically stable, but that their radioactivity is due to the disturbing action of an external field of force originating in the surrounding electrons. The orbits of these may approach very close to the nucleus in heavy elements. A rotation of the nucleus as a whole is postulated and it is pointed out that the frequency of this rotation may be comparable with some electronic frequency and so give rise to destructive perturbations. Nuclear structure is also discussed by W. van der Berg [53] and M. C. Neuberger.[54] Fr. L. Meitner [55] has examined the β-ray magnetic spectrum of uranium-*X*, and finds it to consist of three sharp lines and a faint band. From measurements of these, she concludes that the primary β-rays are emitted from the nucleus with a definite velocity, which is in agreement with the suggestion of Rosseland [56] that an excited atomic system can pass to an unexcited state by the emission of one of its particles in the form of a corpuscular ray as an alternative to the emission of radiation. In a later paper,[57] she discusses the work of Compton [58] and of Debye [59] on the scattering of *X*- and γ-rays by matter as giving a possible explanation of the continuous β-ray spectrum.

The alternative theory of Ellis, which is that the sharp lines of the magnetic spectrum are caused by the action of primary nuclear γ-rays on electrons in different quantum levels outside the nucleus, and that the primary γ-ray may be caused by the passage of an α-particle from one quantum level to another in the nucleus, has received much experimental support. Rutherford, in his discussion on the nucleus of the atom,[60] shows that it is in good accord with his own conclusions that the α- and β-particles liberated from elements of the type of radium-*C* and thorium-*C* may exist as satellites of a core or inner nucleus which is common to both elements.[61] C. D. Ellis and H. W. B. Skinner [62] have determined the absolute energies of the β-ray groups from radium-*B* and -*C*

[52] *Nature*, 1923, **111**, 357; *A.*, 1923, ii, 366.
[53] *Chem. Weekblad*, 1923, **20**, 54; *A.*, 1923, ii, 232.
[54] *Ann. Physik*, 1923, **68**, 574; **70**, 139; *A.*, 1923, ii, 145, 400.
[55] *Z. Physik*, 1923, **17**, 54; *A.*, 1923, ii, 675.
[56] *Ibid.*, 1923, **14**, 173.
[57] L. Meitner, *ibid.*, 1923, **19**, 307; *A.*, ii, 12.
[58] *A.*, 1921, ii, 366.
[59] *Physikal. Z.*, 1923, **24**, 161.
[60] *Roy. Inst.*, April 4, 1924. [61] F. W. Aston, *Nature*, 1924, **113**, 393.
[62] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 60, 165; *A.*, ii, 85, 137.

correct to 1 in 500. The results for 47 lines are tabulated and confirm the conclusion that the groups are due to the conversion of the γ-rays in the various electronic levels. Although the majority of the β-ray lines from radium-*B* (atomic number 82) are due to conversion in atoms of this number, a group of lines of low energy has been found to be due to conversion in atoms of atomic number 83. A more detailed study [63] of the frequencies of the γ-rays confirms the original view that these are due to the transitions between stationary states in the nucleus itself, the evidence being strongly in favour of the hypothesis that the dynamics of the nucleus can be interpreted in terms of the quantum theory.

In a later paper,[64] Ellis describes an accurate redetermination of the high energy groups of the magnetic β-ray spectrum of radium-*C*. He was able to account for all the β-ray lines as being due to quantum conversions in the electron structure. This result is interesting, because the γ-rays concerned are of very high frequency corresponding to potential differences of 1·5 to 2 million volts. It is a striking thing that no fresh absorption phenomena are found even with γ-rays of the highest frequency yet measured. A table of 11 γ-rays is given and a set of nuclear levels suggested, transitions between which are supposed to be the cause of these emissions. In a series of papers,[65] Thibaud describes experiments leading to conclusions of the same general nature. He was not able to proceed to the detailed analysis of the spectrum, as sufficiently accurate measurements were not at his disposal. He appears, however, to have improved the technique sufficiently to obtain direct evidence of the photoelectric groups liberated by the very high frequency γ-rays from ordinary elements.

The magnetic β-ray spectrum of mesothorium-2 has been studied by D. Yovanovitch and J. d'Espine,[66] and later and more completely by D. H. Black,[67] who tabulates values of energies for 31 lines. The grouping of these is in excellent agreement with the theory of Ellis, but from the numerical results it is impossible to decide with certainty whether 89 or 90 is the atomic number concerned in this case.

Ranges of α-Rays.

Continuing her work on the α-rays of polonium, Mlle Curie [68] has now studied their ranges by direct photography of their tracks

[63] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 185; *A.*, ii, 137.
[64] *Proc. Camb. Phil. Soc.*, 1924, **22**, 369.
[65] *Compt. rend.*, 1924, **178**, 1706; **179**, 165; *A.*, ii, 514, 717.
[66] *Ibid.*, 1924, **178**, 1808; *A.*, ii, 447.
[67] *Proc. Roy. Soc.*, 1924, [*A*], **106**, 632.
[68] *Compt. rend.*, 1923, **176**, 434; *A.*, 1923, ii, 207.

in a Wilson expansion chamber. As the density of the gas in the chamber at the moment of emission cannot be stated precisely, the measurements are essentially a comparison of the lengths of tracks obtained at the same instant. Statistical curves connecting the number of the tracks and their lengths are given which show that about 90% of the rays have ranges between $l - 1$ and $l + 1$ mm., where l is the most probable length, and also that it is possible to define an extrapolated trajectory, p, in the same manner as Henderson defines it for the ionisation curve.[69] The relation between these two lengths is $p = l + 0{\cdot}7$ mm., so that, taking Geiger's value for p [70] of 3·92 cm., the most probable length of trajectory will be 3·85 cm. in air at 15° and 760 mm. The ionising power of an α-ray appears to increase at first, pass a maximum 4—3 mm. from its end, and then decrease rapidly during the last few millimetres. The ratio of the extrapolated ranges of radium-*C* and polonium is given as 1·775 : 1, identical with that given by Geiger (*loc. cit.*).

B. Gudden [71] has determined the ranges of uranium-I and uranium-II by measurement of the pleochroic haloes of fluorspar. These correspond to ranges in air of 2·68 and 2·76 cm., respectively. He calculates a new value for the radioactive constant for U-II of $1{\cdot}8 \times 10^{-16}$ sec.$^{-1}$, much smaller than that hitherto accepted, and concludes that the Geiger-Nuttall relation is not satisfied by these bodies.

The ranges of α-particles in the inert gases have been measured by L. F. Bates,[72] using rays of a mean effective range of 4·15 cm. The mean pressures giving the same extrapolated range, and the corresponding stopping powers are tabulated as follows :—

Gas.	Air.	He.	Ne.	A.	Kr.	Xe.
Mean pressure	348·9	—	595·1	375·0	262·2	193·3
Stopping power	1	0·1757	0·586	0·930	1·330	1·804

The stopping power of helium, which for an α-ray from radium-*C* would have a range of nearly 40 cm., had to be measured in a special apparatus. The value for the stopping power calculated by the theory of Henderson [73] in every case but helium accounts for 0·75 of that observed. It is suggested that the difference may be due to multiple ionisation.

Capture and Loss of Electrons by α-Particles.

α-Particles are capable of capturing one or even two electrons during their passage through matter and so becoming singly charged

[69] *Phil. Mag.*, 1921, [vi], **42**, 538; *A.*, 1921, ii, 617.
[70] *Z. Physik*, 1922, **45**.
[71] *Ibid.*, 1924, **26**, 110; *A.*, ii, 717.
[72] *Proc. Roy. Soc.*, 1924, [*A*], **106**, 622.
[73] *Phil. Mag.*, 1922, [vi], **44**, 680.

or neutral. G. H. Henderson [74] was able to photograph a band due to singly charged particles half-way between the normal band and the undeflected band in the magnetic spectrum of α-rays from radon. The subject has been discussed by Bergen Davies [75] and more completely studied by Rutherford.[76] The latter used α-rays from radium-*B* and -*C* in his experiments and counted the particles, after magnetic deflection, by the scintillation method. The velocity of the α-particles is reduced by mica screens and the observation consists in counting the number of singly charged and neutral particles as the pressure is raised from a very low value upward in the deflection apparatus. It is found that the numbers fall off almost exponentially with the increase of pressure, and it can thence be deduced that for an α-particle of velocity $0{\cdot}85 \times 10^9$ cm./sec. the mean value of the free path for loss of an electron is 0·005 mm. and for capture 0·037 mm. in air at *N.T.P.* The ratio of the mean free path for capture to that for loss varies as $V^{4{\cdot}6}$, where V is the velocity of the particle. A complete statistical theory for these phenomena has been worked out by R. H. Fowler.[77]

Radioactive Constants.

The number of α-particles emitted by 1 g. of radium without disintegration products has been carefully redetermined by H. Geiger and A. Werner,[78] using a scintillation method designed to eliminate error as far as possible. They obtain a value $3{\cdot}40 \times 10^{10}$, which is compared with Rutherford and Geiger's value, $3{\cdot}57 \times 10^{10}$, and Hess and Lawson's value of $3{\cdot}72 \times 10^{10}$, and the reasons for the discrepancy are discussed. Using their own value, and Millikan's figure for the charge on the electron, the half-period of radium is calculated to 1730 years and the evolution of helium to 159 cu. mm. per year per gram of radium in equilibrium with radon, radium-*A*, and radium-*C'*. The heat evolved from 1 g. of radium without disintegration products is calculated as 22·25 cal./hour. Comparing this value with the experimental values 25·2 and 25·1 obtained by Rutherford and Hess, respectively, it appears likely that in radioactive changes of the radium atom, in addition to the kinetic energy of the α-particles and recoil atoms, other quantities of energy must be set free in consequence of the changes in the atomic nucleus. This work is criticised unfavourably by V. F. Hess and R. W. Lawson.[79]

[74] *Proc. Roy. Soc.*, 1923, [*A*], **102**, 496.
[75] *Nature*, 1923, **111**, 706; *A.*, 1923, ii, 453.
[76] *Phil. Mag.*, 1920, [vi], **47**, 277; *A.*, ii, 225.
[77] *Proc. Camb. Phil. Soc.*, 1924, **22**, 253.
[78] *Z. Physik*, 1924, **21**, 187; *A.*, ii, 226.
[79] *Ibid.*, 1924, **24**, 401; *A.*, ii, 587

The constant of polonium has been measured by Mlle St. Maracineanu,[80] who obtains a value 139·5 days for the half-change period, the radioactive constant λ being $4{\cdot}96 \times 10^{-3}$ (day)$^{-1}$.

The period of protoactinium has been determined by J. H. Mennie [81] by the comparison of the α-ray activities of ionium and protoactinium separated from several kilograms of uranyl nitrate. He finds the average life period to be 18,000 years in agreement with the period of half-change, 12,500 years, found by Hahn and Meitner.[82]

J. C. Jacobsen,[83] by observing the scintillations from a preparation of pure radium-*C'*, finds a value for its transformation constant λ of $8{\cdot}4 \times 10^5$ sec.$^{-1}$, a value widely different from that calculated by the Geiger and Nuttall relation.

The radioactive constant of radon has been determined by an entirely new method by Mlles I. Curie and C. Chamie,[84] who give a value $3{\cdot}823 \pm 0{\cdot}002$ days. This is compared with the earlier values of Mme Curie and Rutherford, 3·85 days, and the recent determination by Bothe and Leechner, 3·810 days.

Absorption and Scattering of γ-Rays.

The absorption of the penetrating γ-radiation from radium-*B* and -*C* by a number of different metals has been measured by N. Ahmad,[85] who finds that it can be expressed by the formula $1{\cdot}68 \times 10^{-25}Z + 1{\cdot}60 \times 10^{-31}Z^4$, where Z is the atomic number. Slight deviations occur after copper and mercury. Comparison with the corresponding formula for *X*-ray absorption suggests that the first term represents an apparent absorption due to scattering, whilst the second term represents a true absorption. Two independent calculations are made of the effective mean wave-length of the hard γ-rays. These give values 0·015 Å. and 0·019 Å. in good agreement with the determinations made by Ellis.[86]

In a later paper [87] the results are discussed mathematically with special reference to apparent absorption due to scattering. It is found that the total absorption may be represented by the formula $0{\cdot}29\sigma_0 Z + 2{\cdot}29 \times 10^{-2}\lambda^3 Z^4$, where σ_0 is the scattering per electron calculated on the classical theory, Z is the atomic number, and λ is the mean effective wave-length, taken as 0·019 Å. as an upper

[80] *Compt. rend.*, 1923, **176**, 1879; *A.*, 1923, ii, 529.
[81] *Phil. Mag.*, 1923, [vi], **46**, 675; *A.*, 1923, ii, 719.
[82] *Ber.*, 1921, **54**, [*B*], 69; *A.*, 1921, ii, 150.
[83] *Phil. Mag.*, 1924, [vi], **47**, 23; *A.*, ii, 142.
[84] *Compt. rend.*, 1924, **178**, 1808; *A.*, ii, 447.
[85] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 507; *A.*, ii, 440.
[86] *Ibid.*, 1922, [*A*], **101**, 1; *A.*, 1922, ii, 339.
[87] N. Ahmad and E. C. Stoner, *ibid.*, 1924, [*A*], **106**, 8; *A.*, ii, 582.

limit. The scattering per electron is approximately constant over a large angle and is therefore independent of the position and binding of the electron. These results agree qualitatively, but not quantitatively, with Compton's formula. In a more recent paper,[88] Owen describes similar measurements, but not only does he measure the total absorption (scattering plus energy absorption) but by a special experimental arrangement he was able to measure the true energy absorption independently of that due to scattering. He finds the true energy absorption to consist of the sum of two terms, one varying as Z^4 and the other as Z. It is interesting to note that Compton's theory suggests just such a variation.

Another interesting observation connected with the mechanism of scattering has been made by D. Skobelzyn,[89] who has examined the tracks of electrons liberated by γ-rays in a Wilson cloud chamber. He finds that these have velocities corresponding with ranges of about 1 cm. These velocities are much less than those which an electron should attain by the absorption of a complete quantum of the γ-radiation. The directions of motion of the electrons do not in general coincide with the path of the incident γ-rays. The observation is in favour of the Debye-Compton theory of scattering; on the basis of this, it can be explained as a recoil effect, the scattered radiation not being in the form of a spherical wave.

*Number of γ-Rays emitted from Radium-*B *and -*C.—A. F. Kovarik[90] has redetermined the total number of γ-rays emitted per second from radium-*B* and -*C* in equilibrium with 1 g. of radium. This he gives as $7{\cdot}28 \times 10^{10} \pm 0{\cdot}3\%$. Each radioactive transformation results in the emission of one γ-ray entity, which produces a β-ray emission from a single atom. The utmost confidence may be placed in the results of this admirable piece of work. In it the author redetermined every constant used in his calculations, excepting the coefficient of absorption in air, and allowed for every possible correction likely to affect the result.

Uranium and its Relations to Other Elements.

The discovery of uranium-*Z* by Hahn was mentioned in the previous report. A further account of this substance is given by its discoverer,[91] in which a method is described for the determination of the relation of the activity of uranium-*Z* to that of uranium-*X*.

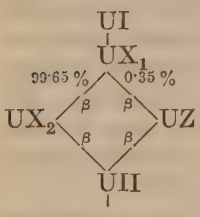
[88] E. A. Owen, N. Fleming, and W. E. Page, *Proc. Physical. Soc.*, 1924, **36**, 355.

[89] *Z. Physik*, 1924, **24**, 393; *A.*, ii, 582.

[90] *Physical Rev.*, 1924, **23**, 559; *A.*, ii, 447.

[91] O. Hahn, *Z. physikal. Chem.*, 1923, **103**, 461; *A.*, 1923, ii, 111

This method he has applied to a large number of uranium-X preparations of different ages and has obtained a satisfactory constant value for the relationship. The constancy of the value allows it to be concluded that uranium-X_1 is the parent substance of uranium-Z. Uranium-X_1, therefore, undergoes a dual β-ray disintegration of a kind which has hitherto not been observed with radioactive elements. A new method of detecting uranium-Z is described and from the activity ratio uranium-Z : uranium-X it is shown that the branching relationship is about 0·35%. The most probable disintegration scheme is as shown in the annexed diagram.



A. S. Russell [92] confirms Hahn's conclusions. He determines the periods of uranium-Y, uranium-Z, and uranium-X_2 to be 25·5 hours, 6·69 hours, and 70·5 seconds, respectively, and points out that the branching ratio given by Hahn is approximately equal to the reciprocal of the periods of the two substances formed, namely, uranium-X_2 and uranium-Z. W. P. Widdowson and A. S. Russell [93] have carefully repeated the work of Boltwood [94] on the relative activities of the radioactive constituents of an unchanged primary uranium mineral (pitchblende). The results indicate, as before, the lowness of the relative activity of the mineral to that of its uranium content, but the new values of the relative activities of polonium, ionium, radium, and uranium are not the same as those previously obtained and now agree closely with those deduced theoretically. In two papers on the radioactive disintegration series, Russell concludes that these are limited to four in number, the members of which have atomic weights given respectively by $4n + 3$, $4n + 2$, $4n + 1$, and $4n$, where n is an integer. He gives reasons for supposing that the first of these is the actinium series, the second the uranium series, the third a hypothetical series the end products of which may be isotopes of bismuth and of thallium, and the fourth the thorium series. The first of the papers [95] is principally concerned with the origin of actinium. From the consideration of simple empirical relations holding among the known radioactive series, he draws the conclusion that actinium arises from an isotope of uranium with an atomic weight 239 present to the extent of about 5%. The disintegration of this is summed up in the following table :—

[92] *Nature*, 1923, **111**, 703; *A.*, 1923, ii, 497.
[93] *Phil. Mag.*, 1923, [vi], **46**, 915; *A.*, 1923, ii, 819.
[94] *Amer. J. Sci.*, 1908, [iv], **25**, 269; *A.*, 1908, ii, 454.
[95] A. S. Russell, *Phil. Mag.*, 1924, [vi], **46**, 642.

Position.	Element.	Period.	z.	Radiation.	a.
(1)	Actinouranium-I	*ca.* 8×10^9 years	92	α	239
(2)	Uranium-Y_1	28 hours	90	β	235
(3)	Uranium-Y_2	*ca.* 1 minute	91	β	235
(4)	Actinouranium-II	2×10^6 years	92	α	235
(5)	Parent of protoactinium	20 years	90	β	231
(6)	Protoactinium	$1{\cdot}2\times10^4$ years	91	α	231
(7)	Actinium	20 years	89	β	227
(8)	Radioactinium	19·5 days	90	α	227

In the second paper,[96] the possibilities of the hypothetical third series are investigated. A large number of experiments were carried out with pitchblende, thorianite, and a preparation of radium in search for the hypothetical isotope of radon, thoron and actinon expelling α-particles and having an anticipated period of 70 minutes. These were completely unsuccessful. It is shown to be theoretically probable that there are only three out of the four possible radioactive series which have members of atomic number 86 emitting α-particles. The fourth, if it exists, should arise from an isotope of protoactinium having an atomic weight of 233, pass through the missing elements 87 and 85, and end in bismuth. The relation between uranium and radium is further discussed by Soddy,[97] who has redetermined the average life period of ionium, from the rate of growth of radium in uranium preparations, as $1{\cdot}08\times10^5$ years, a value 8% higher than that obtained before.[98] Examination of two specimens of ionium–thorium separated from different products from Joachimsthal pitchblende showed an ionium–thorium ratio of 1 : 0·9 in agreement with the latest value given by Meyer and Ulrich.[99]

Radioactivity of the Alkali Metals.

The feeble $\beta\gamma$-radioactivity of the alkali metals has been studied by G. Hoffmann.[1] He describes two very sensitive methods. In the first, the disturbance due to α-radiation is avoided by placing the ionisation chamber at a sufficient distance from the substance. The second method is for use when there are no α-rays or so few that the $\beta\gamma$-radiation can be measured between these occurrences with sufficient accuracy. These methods have been applied to the alkali metals with results in good agreement with those obtained previously by Hahn and Rothenbach.[2] The activities of sodium

[96] W. P. Widdowson and A. S. Russell, *ibid.*, 1924, [vi], **48**, 293; *A.*, ii, 649.

[97] F. Soddy and A. F. R. Hitchens, *ibid.*, 1924, [vi], **47**, 1148; *A.*, ii, 446.

[98] Soddy, *ibid.*, 1919, [vi], **38**, 483; *A.*, 1919, ii, 443.

[99] *Sitzungsber. Akad. Wiss. Wien*, 1923, **132**, 279.

[1] *Physikal. Z.*, 1923, **24**, 475; *A.*, ii, 86; *Z. Physik*, 1924, **25**, 117; *A.*, ii, 718.

[2] *Physikal. Z.*, 1919, **20**, 194; *A.*, 1919, ii, 312.

and cæsium are found to be negligible. The ratio of the $\beta\gamma$-activities of potassium and rubidium is found by the first method to be 1 : 4, by the second to be 1 : 7·6. The ratio of the $\beta\gamma$-activity of potassium to that of uranium is given as 1 : 460. These feeble radioactivities are particularly interesting in connexion with the isotopic constitutions of the alkali metals. Their complete absence in the two simple ones appears significant. The activity in potassium and rubidium may be general or confined to one of their known isotopes, or alternatively it may be entirely due to the presence of minute traces of unknown radioactive isotopes. It is worth noting that the ratio of activity given above is about the same as the ratio of the percentage of the less abundant isotopes, K^{41} and Rb^{87}, in these two elements.

F. W. Aston.

COLLOID CHEMISTRY.*

Theoretical papers on the colloidal state have appeared by several authors. P. Bary [1] discusses the two schools of thought: the 'physical' theory of colloids, and the 'chemical' theory. On the one hand, colloidal properties are considered to arise within a certain range of dispersion, *i.e.*, colloidality is merely a state of matter. Bary and the 'chemical' school would term colloidal those substances which readily polymerise, swell in certain liquids, are amorphous, and exhibit somewhat vague chemical reactions.

P. P. de Weimarn [2] gives a review of his work under the title "Some Fundamental Principles of my Theory of the Colloidal State." This is simply a summary of his well-known views on colloidal dispersion, and his laws of corresponding states. He believes that "all those physical and chemical properties which one specifically associates with colloidal substances, appear spontaneously for *each* solid substance on progressive dispersion to the requisite degree, no matter how the dispersed state is reached." M. J. Duclaux [3] prefers a different view from that of de Weimarn: "true colloids are distinguished by the fact that their molecules can assume considerable dimensions by simply calling into play principal valencies. They can condense, but crystalloids cannot."

Reviewing his work on sulphur sols (A., 1914, ii, 35; 1915, ii, 97, 152; 1922, ii, 485; 1924, ii, 330), G. Rossi [4] discusses the colloid state, giving a theory as to the origin of suspensoids and emulsoids, and why a given substance may form a colloid in one solvent and a true solution in another. He believes that colloidal dispersion is maintained by other forces than that of the simple affinity of the solvent for the solute. For colloidal suspensoid systems, such affinity is slight, if any, and electric charges play the dominant *rôle*. For emulsoid systems, the solvent promotes dispersion and stability to a certain extent, the electric charge assisting stability.

* This Report has been prepared on behalf of the British Association Committee on Colloid Chemistry (Prof. F. G. Donnan, Chairman; Dr. W. Clayton, Secretary; Mr. E. Hatschek; Prof. J. W. McBain; Prof. W. C. McC. Lewis) by the Secretary. The section on gels and Liesegang phenomena is contributed by Mr. Emil Hatschek.

[1] *Rev. gén. Coll.*, 1924, **2**, 33; *A.*, ii, 239.

[2] *Ibid.*, pp. 193, 225; *vide* also *Bull. Soc. chim.*, 1924, [v], **35**, 530.

[3] *Rev. gén. Coll.*, 1924, **2**, 257.

[4] *Gazzetta*, 1924, **54**, 227; *A.*, ii, 459.

The work of W. Pauli and his collaborators since 1917 on the structure of colloids has been reviewed in detail by him.[5]

An interesting paper on the theory of colloid phenomena has appeared by U. R. Evans and L. L. Bircumshaw,[6] who point out that forces of electrical origin exist at the interface: colloid–liquid medium. In addition to interfacial tension acting *along* the interface, there are forces acting *across* the interface, *i.e.*, perpendicular to the boundary. Such "adhesive forces" binding the colloid and medium together are high when the interfacial tension is low and *vice versa*. At or near the isoelectric point, where interfacial tension is a maximum, the adhesive forces are a minimum, so that stability, peptisation, and swelling are at a minimum too.

The Brownian movement of the same particles at various pressures has been investigated by S. Landman,[7] who finds more active motion as the pressure decreases. The ageing of colloidal solutions is discussed by H. Gessner,[8] who worked with vanadium pentoxide sols. His paper is too long for adequate summary here. The influence of colloids on the rate of reactions involving gases has been further studied by A. Findlay and W. Thomas.[9] They used sols of gelatin, starch, dextrin, albumin, and peptone as the colloids and the reactions chosen were the decomposition of hydrogen peroxide by fuller's earth, of nitrosotriacetonamine in the presence of hydroxyl ion, and of hydrogen peroxide in presence of iodide ion.

The possibility of a connexion between the protective effect of gelatin and other 'schutz' colloids and their elastic properties is mooted by H. Freundlich and J. F. Loeb.[10] The properties of the colloids sodium stearate and sodium oleate support that view.

A capillary viscosimeter has been described by W. Ostwald[11] which permits definite values for the viscosity of colloidal solutions. Using the Hess and Couette viscosimeters, H. Freundlich and E. Schalek[12] found that sols of As_2S_3, ZrO_2, CaF_2, and S obeyed Poiseuille's law, but sols exhibiting a marked elasticity showed wide deviations from this law. As example, sodium stearate in 0·1% solution showed marked elasticity and did not obey Poiseuille's law, whilst sodium oleate up to 40% solution showed no elasticity and obeyed Poiseuille's law. The theory of the elasticity of colloidal solutions is worked out by A. Szegvari.[13]

The Mie-effect (*Ann. Physik*, 1908, [iv], **25**, 37) has been studied

[5] *Naturwiss.*, 1924, **12**, 421.
[6] *Kolloid. Z.*, 1924, **34**, 65; *A.*, ii, 236.
[7] *Z. Physik*, 1924, **27**, 237.
[8] *Koll. Chem. Beihefte*, 1924, **19**, 213; *A.*, ii, 741.
[9] *J.*, 1924, **125**, 1244.
[10] *Kolloid-Z.*, 1924, **34**, 230.
[11] *Z. physikal. Chem.*, 1924, **111**, 62.
[12] *Ibid.*, **108**, 153.
[13] *Ibid.*, **108**, 175.

by Szegvari [14] and by A. Ehringhaus and R. Wintgen.[15] The Mie-effect is the name given to the phenomenon shown when a particle the diameter of which is less than half a light-wave length is illuminated by a beam of light. The light is scattered in all directions, with the greatest intensity in the direction of the primary beam, this being more pronounced as the particle size increases. Szegvari describes ultramicroscopical investigations with unidirectional illumination, whilst Ehringhaus and Wintgen confirm Mie's theory by a photometric estimation of the absorption of monochromatic light illuminating gold suspensions in fused borax.

C. Wha [16] has detailed the technique of ultrafiltration and described a vacuum dialyser made of collodion. The question whether the membranes used in ultrafiltration operate as sieves or by virtue of solubility differences has been raised by J. Duclaux and J. Errera,[17] who carried out an extensive study of the mechanism of ultrafiltration. They conclude that the velocity of filtration is, within a few units per cent., inversely proportional to the viscosity of the liquid and directly proportional to the pressure. Slight variations from this rule may be caused by deformation of the membrane under pressure, swelling of the membrane itself, and by an '*E.M.F.* of filtration,' this disappearing with a conducting liquid no matter what the p_H value. The membrane behaves like a bundle of rigid capillary tubes. Solvation, surface tension, the p_H of the liquid, and the osmotic pressure have only a slight influence on the membrane. This may not be true, however, for membranes of a finer structure, *i.e.*, lesser porosity.

A new ultrafiltration apparatus has been described by H. Bechold and L. Gutlohn,[18] whilst J. A. Pickard [19] has given details of the so-called "stream-line filter" and discussed its application for clarifying spent lubricating oil, varnishes, fixed oils, gums, and glues. Electrodialysis is treated by H. Freundlich and L. F. Loeb.[20]

Under cataphoresis must be mentioned an important paper by L. Michaelis and A. Domboviceanu,[21] who measured the cataphoresis of mastic sols. The relation between the cataphoretic velocity and variations in the electrical properties of the double layer surrounding the particles was investigated, the adsorbed kations being kept all of one kind, *viz.*, by using hydrogen ion as the adsorbed

[14] *Z. Physik*, 1924, **21**, 348; *A.*, ii, 315.
[15] *Z. physikal. Chem.*, 1924, **108**, 406; *A.*, ii, 396.
[16] *Biochem. Z.*, 1924, **144**, 278; *A.*, i, 458.
[17] *Rev. gén. Coll.*, 1924, **2**, 130.
[18] *Z. angew. Chem.*, 1924, **37**, 494.
[19] *J. Oil and Colour Chem. Assoc.*, 1924, **7**, 110.
[20] *Biochem. Z.*, 1924, **150**, 522.
[21] *Kolloid-Z.*, 1924, **34**, 322; *A.*, ii, 738.

kation. The essential fact was established that the cataphroetic velocity increases as the p_H value rises, but by no means to the same extent as would be expected if the cataphoretic potential depended on the p_H value as does the potential of the hydrogen electrode. The potential difference associated with electrokinetic phenomena in colloid systems is not comparable with the Nernst potential difference, *e.g.*, as applied to the pole of a galvanic circuit.

Adsorption and cataphoresis experiments with suspensions of glass and with selenium sols have been published by K. von der Grinten,[22] whose results correspond with the maximum adsorption as a unimolecular film on the particles.

Particle Size.

E. F. Burton and J. E. Currie,[23] continuing the work of Burton and Bishop (*Proc. Roy. Soc.*, 1922, [*A*], **100**, 414) and using sols of gamboge, arsenious sulphide, copper, and silver, conclude that the particles are uniformly distributed in these colloidal solutions. The uniform distribution is probably due to the electrical charges on the particles.

The question of the percentage distribution of particles of definite size in a colloid sol or coarse suspension is very much to the fore just now. C. A. Klein and J. Parrish [24] have published a detailed report of their work on size analysis, with special reference to pigments. Various methods are reviewed and their own elutriation method is given fully. An extension of the Odén recording balance has been developed at the Rothamsted laboratories.[25] The new apparatus is an automatic self-recording balance controlled electromagnetically, and can be used with no loss of sensitivity up to the maximum load the balance is designed to carry. Further, the sensitivity can be very simply adjusted, so that both rapid and slow changes of weight can be recorded.

The Ostwald-von Hahn ' flocculation meter ' (*Kolloid-Z.*, 1923, **32**, 60) has been modified by W. J. Kelly,[26] for determining the distribution of particle size in suspensions. Presupposing the validity of Stokes's law for the rate of settling, the method consists in following the change in hydrostatic balance when the suspension is balanced against the dispersion medium in a U-tube apparatus. The same apparatus has been modified by E. O. Kraemer and A. J. Stamm [27]

[22] *Compt. rend.*, 1924, **178**, 2083; *A.*, ii, 664.
[23] *Phil. Mag.*, 1924, [vi], **47**, 721; *A.*, ii, 459.
[24] *J. Oil and Colour Chem. Assoc.*, 1924, **45**, 54.
[25] J. R. H. Coutts, E. M. Crowther, B. A. Keen, and S. Odén, *Proc. Roy. Soc.*, 1924, [*A*], **106**, 33.
[26] *J. Ind. Eng. Chem.*, 1924, **16**, 928.
[27] *J. Amer. Chem. Soc.*, 1924, **46**, 2709.

to determine the distribution of size of particles in emulsions. Their work is important, as very few studies have been made on the size-analysis in liquid–liquid systems, and a promising line of research is opened up.

M. Mason and W. Weaver [28] have published a mathematical paper on the settling of small particles in a fluid. The outstanding work, however, on this subject is the elaboration of the ultra-centrifuge by The Svedberg and H. Rinde.[29] A specially designed centrifuge enables the changes taking place in a fine-grained sol during centrifuging to be followed photographically or directly by telescope and scale. The mathematical theory underlying this method has been further developed. Thus Stokes's law is modified for the influence of variation of acceleration with distance from the axis of rotation, whilst the theory is given for the determination of distribution of particle size. Results of measurements of size and distribution of size of particle for gold sols of average radius 2·3, 3·6, 7·1, 11·6$\mu\mu$ are given and the nature of the protective action of gelatin upon fine-grained gold sols has been studied. As an instrument of research the ultra-centrifuge promises a brilliant future.

In connexion with particle size attention may be directed to W. D. Bancroft's [30] work on the colour of colloids and the production of Tyndall-blue in solids, and to H. Remy's [31] investigation on the particle size of chemical fumes.

The presence of colloids in solutions which give precipitates on interaction causes smaller particles to be formed. W. G. France and D. McBurney [32] find that as little as 0·013% of gelatin reduces the average size of the particles of basic lead carbonate to approximately one-third the normal size, when sodium carbonate and sodium chlorate together in water are electrolysed between lead electrodes at 20° whilst carbon dioxide is bubbled near the anode. F. J. Brinley [33] reports the similar observation that colloidal arsenate of lead is prepared when lead nitrate and disodium arsenate react in the presence of gelatin and other colloids.

Sols.

The well-known work of Svedberg on the formation of colloids by electrical methods is extended by him in collaboration with E. O. Kraemer.[34] Previous work on the electrical pulverisation of metals in the high-frequency arc suffered from the defect that the

[28] *Physical Rev.*, 1924, **23**, 412. [29] *J. Amer. Chem. Soc.*, 1924, **46**, 2677.
[30] *J. Physical Chem.*, 1924, **28**, 12. [31] *Z. anorg. Chem.*, 1924, **138**, 167.
[32] *J. Amer. Chem. Soc.*, 1924, **46**, 540; *A.*, ii, 314.
[33] *J. Agric. Research*, 1924, **26**, 373.
[34] *J. Amer. Chem. Soc.*, 1924, **46**, 1980; *vide* also R. Fürth, *Kolloid-Z.*, 1924, **34**, 224; *A.*, ii, 533.

generation of the high-frequency oscillations is disturbed and modified by the pulverisation process which takes place in the same circuit and across the same spark gap. Now by the use of a low-voltage type of Tesla coil (which separates these two processes) as a source of damped high-frequency oscillations, cadmium has been dispersed in water, alcohol, and ether, giving much purer sols. Rates of pulverisation, sediment formation, and decomposition of the medium were investigated. The authors also discuss the possible causes underlying the various behaviours of the different electrical circuits, laying stress on the influence of the character of the condenser discharge upon the pulverisation process.

The formation of colloids in the electrolysis of dilute solutions has been studied by P. N. Pavlov.[35] With silver thread electrodes 1—2 mm. apart in water, and a low voltage (2 volts), coloured streams of strong polarity are evidenced, yellowish-green at the cathode and red at the anode. Sols were similarly obtained with iron, gold, and bismuth electrodes, also with copper electrodes in very dilute copper sulphate solution.

Detailed experiments along similar lines have been carried out by V. Kohlschütter,[36] who made ultramicroscopic observations on the processes which occur at the electrodes during electrolysis, whilst F. Thoren [37] has worked on the electrolytic precipitation of nickel in disperse form from an ammoniacal solution of nickel nitrate. He obtained particles about 0·3 to 0·25μ, and apparently they were non-crystalline.

Colloidal gold has been prepared by heating a solution of gold chloride with formaldehyde, neutrality being carefully maintained during the process.[38] P. A. Thiessen [39] has shown that the red hydrosol of gold prepared by the formaldehyde reduction of alkaline gold solutions consists of pure metal ultramicrons free from oxidation products. Partial reduction leading to a blue sol results in ultramicrons of gold and gold oxide. Thiessen cannot substantiate Pauli (*A.*, 1921, ii, 246) that compounds between gold and water exist in the coagula of these sols. Thiessen [40] has also investigated the sensitivity of phosphor-gold hydrosol (Au_p) to ammonia, and shown it to be due to the presence of unreduced gold compounds in the sol.

Using a highly purified gold sol, M. Adolf and W. Pauli's experiments [41] led to the calculation that the sol contained particles of

[35] *J. Amer. Chem. Soc.*, 1924, **46**, 100; *A.*, ii, 236.
[36] *Z. Elektrochem.*, 1924, **30**, 164; *A.*, ii, 538.
[37] *Ibid.*, p. 20
[38] F. T. Grey, *Biochem. J.*, 1924, **18**, 448; *A.*, ii, 460.
[39] *Z. anorg. Chem.*, 1924, **134**, 393; *A.*, ii, 691.
[40] *Loc. cit.*, p. 357; *A.*, ii. 691
[41] *Kolloid-Z.*, 1924, **34**, 29; *A.*, ii, 311.

an average size $27\mu\mu$ (cube edge). From *X*-ray data of Scherer (Appendix to Zsigmondy's "Kolloidchemie," 4 Aufl., 406), it is calculated that each gold particle has 57,000 negative charges.

W. Pauli [42] and R. Zsigmondy [43] have put forward arguments relating to the chemical composition of red gold sols, the former asserting that the gold particles are enveloped with an ionogen complex of a gold sol, whilst the latter believes that this ionogen complex is merely adsorbed water.

Silver sols have been investigated by several workers. E. Erlach and W. Pauli [44] determined the conditions of formation and the composition of the sols produced by Kohlschütter's method (*A.*, 1908, ii, 182). The dialysed sols may contain up to 20% of silver oxide, which may be removed by reduction with hydrogen. Apparently between ten and thirty atoms of silver are associated with one electric charge.

Impure silver sols of low concentration and little stability have been obtained by G. Rebière [45] by grinding precipitated silver in water. Other methods were tried, but silver oxide particles invariably resulted as impurity. A detailed study of colloidal silver with special reference to its therapeutic use has been published by H. Schlee.[46] Medicinal uses of colloidal silver are also dealt with by J. R. Petroff [47] and by Suganuma.[48]

According to G. Rossi,[49] sulphur sols are stabilised by sulphuric acid and sodium sulphate. The quantity of coagula obtained from different sols containing the same percentage of sulphur but different amounts of sulphuric acid and sodium sulphate is inversely proportional to the latter. The great significance of crystalloid stabilisers in colloidal solutions is emphasised.

Colloidal selenium has been prepared by A. Gutbier [50] by reduction of selenium oxide with hydrazine hydrate, the stabiliser being a dialysed extract of carob-beans. The sol is yellow to dark red, depending on the degree of reduction or concentration. The stability is poor, and electrolytes coagulate the sol rapidly.

A new method of preparing colloidal silicic acid has been elaborated by R. Schwarz.[51] Pure silicic acid gel is treated with $3N$—$5N$-ammonia (100 c.c. of ammonia to 0·4 g. of SiO_2) and allowed to stand 100 hours. Filtration followed by ultrafiltration, and then desiccation in a vacuum over dilute sulphuric acid, gives a water-clear sol of high dispersity. Schwarz carried out precipitation experiments

[42] *Microchemie*, 1924, **2**, 47. [43] *Ibid.*, p. 50.
[44] *Kolloid-Z.*, 1924, **34**, 213; *A.*, ii, 532.
[45] *Rev. gén. Coll.*, 1924, **2**, 105, 139; *A.*, ii, 661.
[46] *Biochem. Z.*, 1924, **148**, 383; *A.*, i, 1262.
[47] *Z. ges. expt. Med.*, 1924, **42**, 242. [48] *Biochem. Z.*, 1924, **144**, 141.
[49] *Kolloid-Z.*, 1924, **34**, 20. [50] *Ibid.*, p. 336; *A.*, ii, 739. [51] *Ibid.*, p. 23.

with sols of iron and aluminium hydroxides, albumin, and human serum. A paper on colloidal silica has also been published by F. Diénert and F. Wandenbulcke.[52]

Vanadium pentoxide sols have been prepared by A. V. Dumanskĭ,[53] employing Biltz's method (*A.*, 1904, ii, 324). The red sols were negatively charged. Conductivity measurements were made under various conditions. Perfectly clear sols did not show the phenomenon of double refraction (Freundlich, *A.*, 1916, ii, 442), but it became well marked in turbid sols or gels. The dielectric constant of vanadium pentoxide sol has been determined [54] for a wave-length of 70 cm. and a 3 years' old sol. Increase in concentration resulted in an enhanced dielectric constant, the converse being true for freshly-made sols. General agreement is found with the results of Errera (*A.*, 1922, ii, 694) for much longer wave-lengths.

The constitution of arsenious sulphide sols has been studied by W. Pauli and A. Semler.[55] The sols were prepared from solutions of glassy arsenic trioxide with hydrogen sulphide and the latter was removed by bubbling hydrogen. Various experimental methods led to a structure being proposed for the colloidal sulphide as $(x\mathrm{As_2S_3},\mathrm{As_2S_4H_2} - \mathrm{As_2S_4H})\mathrm{H}$. A. Semler [56] extended this work to a consideration of the chemical behaviour and colours of the ionogen complexes of arsenic sulphide sols. A theory is put forward that the sol is formed through the production and subsequent decomposition of unstable thioarsenious acid. The conditions governing the size of particles in arsenic sulphide sols made by the action of hydrogen sulphide on solutions of arsenic trioxide have been investigated by methods involving the absorption spectra of the sols and their absorption coefficient for a definite wave-length. A. Boutaric and M. Vuillaume [57] thus find that increase in the particle size follows increased concentration of the arsenious oxide solutions, rise in temperature, excess of hydrogen sulphide, and the use of a slower current of this gas. Flocculation tests with electrolytes were made in relation to particle size.

The experiments of R. Wintgen and H. Löwenthal with chromic oxide sols,[58] confirmed the results of previous work with stannic oxide, ferric oxide, gelatin, and dyestuffs, that the micelle simulates a multiply-charged ion.

The preparation of nickel hydroxide gel by the action of *N*-alcoholic potassium hydroxide on a solution of nickel acetate in

[52] *Compt. rend.*, 1924, **178**, 564; *A.*, ii, 253.
[53] *J. Russ. Phys. Chem. Soc.*, 1924, **54**, 703; *A.*, ii, 195.
[54] R. Fürth and O. Blüh, *Kolloid-Z.*, 1924, **34**, 259; *A.*, ii, 729.
[55] *Ibid.*, p. 145. [56] *Ibid.*, p. 209; *A.*, ii, 532.
[57] *Compt. rend.*, 1924, **178**, 938.
[58] *Z. physikal. Chem.*, 1924, **109**, 378; *A.*, ii, 534.

glycerol has been investigated by O. F. Tower,[59] who proved the composition to be $Ni(OH)_2$, not NiO or an intermediate hydrate.

The constitution and stability of iron oxide sols have been further investigated,[60] dialysis of ferric chloride being employed. The general formula of such a sol is $[x\text{Fe(OH)}_3,y\text{FeOCl,FeO}]\text{Cl}'$. Prolonged dialysis diminishes x, and the sol is less stable.

Aluminium oxide gel has been prepared [61] as follows: 150 c.c. of 0·1*N*-ammonia, ice-cold, were stirred by a stream of air saturated with ammonia, whilst 50 c.c. of 0·1*N*-aluminium chloride solution was added little by little. The fine-grained, milky precipitate was dialysed for 50 hours, when the electrical conductivity was constant at $9{\cdot}88 \times 10^{-6}$ mho. Traces of ammonia peptised the gel completely to an unstable, water-clear, negative sol.

The colloid chemistry of night-blue is dealt with by F. V. von Hahn,[62] whilst H. Freundlich [63] deals with sols of pyrrole-red.

Coagulation.

Smoluchowski's theory (*A.*, 1917, ii, 297) of the coagulation of colloids has been investigated by L. Anderson [64] and by J. N. Mukherjee and S. K. Majumdar.[65] Anderson observed the rate of coagulation of gold sols by hydrochloric acid, potassium chloride, barium chloride, and aluminium chloride. In agreement with previous investigators, a region of rapid coagulation is found in which Smoluchowski's equation holds fairly well. In the case of slow coagulation, as when using dilute solutions of electrolytes, the equation no longer holds. Anderson suggests this may be due to the initial primary gold particles being unequally charged. Slow and eventually incomplete coagulation is due to the adsorption of small amounts of electrolyte, and some of the more highly-charged particles may not adsorb sufficient electrolyte to reduce the charge below the critical limit permitting of coagulation.

Mukherjee and Majumdar studied the rates of coagulation of arsenious sulphide sol in presence of inorganic salts. In the region of slow coagulation, Smoluchowski's equation breaks down after a certain stage of coalescence, and the coalescence stops at a certain stage, depending on the rate of coagulation. The greater this rate, the more advanced is the limiting stage of coalescence. Near this stage and afterwards, Smoluchowski's equation is completely invalid. It is suggested that coalescence is reversible or irreversible, according to the potential of the double layer, the limiting stage

[59] *J. Physical Chem.*, 1924, **28**, 176; *A.*, ii, 237.
[60] W. Pauli and F. Rogan, *Kolloid-Z.*, 1924, **35**, 131; *A.*, ii, 740.
[61] A. Lottermoser and F. Friedrich, *Ber.*, 1924, **57**, [*B*], 808.
[62] *Kolloid-Z.*, 1924, **34**, 162; *A.*, ii, 311. [63] *Ibid.*, p. 257; *A.*, ii, 739.
[64] *Trans. Faraday Soc.*, 1924, **19**, 623; *A.*, ii, 531. [65] *J.*, 1924, **125**, 785.

resulting when there is an equilibrium between the rates of coagulation and the breaking up of the aggregates due to fluctuations in thermal energy. (Smoluchowski's theory and a full discussion of the precipitation of suspensoids by electrolytes have been dealt with by Mukherjee in a Thesis, Calcutta University Press, 1924.)

Primarily to ascertain whether the "activity" of ions rather than their concentration plays the significant *rôle* in electrolytic coagulation of colloids, Anderson [66] investigated the effect of sucrose on the rate of coagulation of gold sols by hydrochloric acid, potassium chloride, and barium chloride. Sucrose increases the "activity" of various ions whilst not appreciably altering their concentrations. The general conclusion was drawn that the coagulating power of an ion is dependent on its "activity" rather than on its concentration. Incidentally, it was found that sucrose exerts a definite peptising effect on colloidal gold.

The kinetics of coagulation have also been studied by H. H. Paine and G. T. R. Evans,[67] who followed the coagulation of colloidal copper hydroxide by potassium sulphate. Freundlich's extension (*A.*, 1919, ii, 53) of Smoluchowski's theory led to an equation for the rate of coagulation which required that, as the concentration of the electrolyte increases, the rate of coagulation should approach a certain limiting value. The results of Paine and Evans agree closely with Freundlich's equation and they confirm the existence of a maximum rate of coagulation. On the experimental side, the interesting feature of this work was the use of a protective colloid (soluble starch) to retard coagulation. Thus very rapid coagulations could be brought into the region of observation by ordinary methods, whilst a "transformation factor" permitted the calculation of the rate of coagulation for the pure colloid.

The mechanical condition of coagula has been investigated by S. S. Bhatnagar, K. K. Mathur, and D. L. Shrivastava.[68] Using sols with uniform particles obtained by ultrafiltration, they found the coagula also consisted of uniform particles. An elutriation method was employed to determine particle size. When the sols were coagulated by uni-, bi-, and ter-valent ions, respectively, the greatest elutriation velocities required to separate the particles of final size from the coagula were approximately in the ratio 1 : 2 : 3. This result favours the electrical adsorption theory of coagulation.

J. N. Mukherjee and B. C. Roy [69] have published the results of an investigation confirming and extending the well-known views of the

[66] *Loc. cit.*, p. 635; *A.*, ii, 531.
[67] *Trans. Faraday Soc.*, 1924, **19**, 649; *A.*, ii, 531.
[68] *J. Physical Chem.*, 1924, **28**, 387; *A.*, ii, 395. [69] *J.*, 1924, **125**, 476.

first author relating to the electro-kinetics of coagulation of sols by electrolytes: a reversal of the charge of the surface (colloid particle) is possible by electrical adsorption only when the valency of the oppositely charged ion is greater than that of the ions to the primary adsorption of which the surface owes its charge. When the oppositely charged ion is acted upon by chemical affinity of the surface atoms, a reversal in charge is possible independent of its valency. The alkali-metal kations can never reverse the charge of colloidal surfaces, as they are univalent, and their chemical behaviour may be summed up in their tendency to exist as ions. The alkaline-earth metal ions also are not likely to be chemically or primarily adsorbed. Unless the primarily adsorbed ions are univalent, an alkaline-earth metal ion cannot reverse the charge by electrical adsorption.

Using negatively charged sols of arsenious sulphide, mercuric sulphide, sulphur, gamboge, and mastic, a large number of inorganic and some organic electrolytes were tried. In no case was a reversal of sign obtained with the kations H, Li, Na, K, Rb, Cs, Ca, Ba, even although in some cases saturated solutions were used.

K. C. Sen, P. B. Ganguly, and N. R. Dhar [70] have investigated the coagulation of negative and positive sols of ferric hydroxide, and of negative antimony sulphide sol by electrolytes. Quite a number of interesting results were obtained. Thus when the concentration of the sol is changed, the order of the coagulative powers of different electrolytes alters. Again, in determining the coagulative powers the effect of the opposite ion must be considered. In the case of the positively charged ferric hydroxide sol (anionic coagulation), the Schulze-Hardy law of coagulative powers is borne out. On reversing the charge on the sol, the order of the precipitating ions is reversed.

In the majority of cases, the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation. Certain conclusions of E. F. Burton (*J. Physical Chem.*, 1920, **24**, 701; 1921, **25**, 517) are questioned.

An investigation on the coagulation of negatively charged gold sols has been made by D. C. Henry and V. A. Morris,[71] who used a series of salts of the same kation (sodium), with a view to ascertain the relative stabilising powers of the various anions, a point which has received little attention hitherto. The results indicate the following sequence of stabilising power of various anions when associated with sodium ion in the coagulation of a gold sol: oxalate > HPO_4'' > CO_3'' > OH', citrate > HCO_3' > Br', I', acetate, valerate > butyrate, CNS' > SO_4'' > Cl', benzoate. The ionic series

[70] *J. Physical Chem.*, 1924, **28**, 313. [71] *Trans. Faraday Soc.*, 1924, **20**, 30.

deduced by various workers for adsorptive and coagulative processes indicate ionic adsorption to be highly specific to the adsorbent.

The influence of anions on the coagulation of negatively charged suspensions (sols of arsenious sulphide and gold) with various alkali metals and with acids is dealt with by J. N. Mukherjee and S. G. Chaudhuri.[72] In the case of Cl', Br', NO_3', and SO_4'', the anions have little influence, but complex anions such as benzoate, ferricyanide, or salicylate exert a marked influence, a higher kation concentration being necessary for coagulation.

The actual coalescence of particles when a gold sol and a chromic oxide sol are mixed together has been described by R. Wintgen and H. Löwenthal,[73] who followed the coagulation process by means of an immersion ultramicroscope. The same authors [74] have investigated the mechanism of the reciprocal precipitation of colloids, using stannic oxide, peptised with alkali, and chromic oxide sols. Precipitation occurred only within narrow limits and with a pronounced maximum (as shown by the absence of a "Tyndall beam"). Without regard to the dilution of the sols before mixing, the maximum precipitation occurred when the proportions were as calculated from the theory that such reciprocal precipitation is a maximum when the concentrations of the sols, expressed in gram-equivalent aggregates per litre, are the same. ("Equivalent aggregate" = the weight of a particle divided by the number of its charges.)

When an electrolyte is added to a colloidal suspension, but in amount too small to effect coagulation, a definite degree of protection is sometimes conferred on the suspension. A. Boutaric and Mlle G. Perreau [75] have worked on this matter. The rate of coagulation of colloidal sols to which numerous electrolytes were added was followed by measuring the absorption of monochromatic light (*A.*, 1921, ii, 537). When part of an electrolyte solution is added to the sol, and after some time the remainder is added, the rate of coagulation is less than if all the electrolyte were added at once. The greater the amount of the first addition and the longer the interval between the additions, the more pronounced is the retardation of coagulation. If the two additions are made with different electrolytes, a protective effect is seen in some cases, but in others an acceleration occurs. Although the protective action was observed with mastic and gamboge suspensions, arsenious sulphide sols did not so respond.

[72] *J.*, 1924, **125**, 794.
[73] *Kolloid-Z.*, 1924, **34**, 296; *A.*, ii, 739.
[74] *Z. physikal. Chem.*, 1924, **109**, 391; *A.*, ii, 535.
[75] *Compt. rend.*, 1924, **179**, 46; *A.*, ii, 595.

K. C. Sen [76] has dealt with the peptising influence of benzoic, acetic, and propionic acids on aluminium hydroxide sols. The most effective peptising acid is benzoic, this being the acid most readily adsorbed. As the acid concentration is increased, the stability of the sol increases to a maximum. For sols of the same degree of purity, the greater the dilution the less the stability.

J. Oliver and L. Barnard [77] have an interesting paper dealing with the influence of electrolytes on the stability of red blood-corpuscle suspensions. Later,[78] they contrasted the effect of the valency of kations on negatively charged cells with the effect of the valency of anions on positively charged cells.

Emulsions.

Comparatively few papers have appeared during 1924 marking progress in this field.

W. D. Harkins and E. B. Keith [79] give a very condensed statement of the experiments made to support the oriented wedge theory of emulsions. Where soap is the emulsifying agent, the factor determining the size of dispersed oil globules in water is the shape of the soap molecule. Inversion of an oil-in-water emulsion to the water-in-oil type caused by the addition of the salt of a bivalent metal is due to the great increase in cross-section of the oil-like end (compare Finkle, Draper, and Hildebrand, *J. Amer. Chem. Soc.*, 1923, **45**, 2780). It is found that the size of the oil globules depends on the nature of the oil and on mechanical factors such as the degree of mixing.

P. A. van der Meulen and W. Rieman [80] have investigated monomolecular films of sodium ricinoleate in emulsions, the object being to determine the average area of interface covered by a molecule of sodium ricinoleate in emulsions of a phenol–toluene mixture in water. Keeping the ratio of the internal to external phase practically constant (1 : 54), but varying the concentration of the soap present in the external phase, it was found that the average area of interface covered by a molecule of the soap is a function of the soap concentration. Assuming that with dilute soap solutions the adsorbed molecule lies flat in the interface, but that in more concentrated solutions the CO_2Na group only is in the interface (the remainder of the molecule being in the oil phase), the authors conclude that the average area of interface per adsorbed molecule of sodium ricinoleate varies between 22 sq. Å. and 111 sq. Å. The former value is the cross-section area of the carboxyl group

[76] *J. Physical Chem.*, 1924, **28**, 1029; *A.*, ii, 830.
[77] *J. Gen. Physiol.*, 1924, **7**, 99; *A.*, ii, 831.
[78] *Loc. cit.*, p. 225. [79] *Science*, 1924, **59**, 463; *A.*, ii, 730.
[80] *J. Amer. Chem. Soc.*, 1924, **46**, 876; *A.*, ii, 389.

and the larger value is the cross-section area of a molecule of ricinoleic acid.

S. S. Joshi [81] finds that the surface tension of emulsions of oil in water, no free oil or other impurities being present, is identical with that of the water. Similarly, the surface tension of an emulsion of oil in sodium oleate solution is identical with that of the soap solution alone. Again, when castor or olive oil is the dispersion medium, water being present as the emulsified globules, and soap is the emulsifying agent, the surface tension of the emulsion is practically that of the oil. Thus the inversion point of an emulsion may be determined by noting when a sharp change in surface tension occurs during the treatment of the emulsion, *e.g.*, on addition of electrolytes.

M. H. Fischer still emphasises the resemblance of soap solutions to emulsions such as phenol and water,[82] or to a gelatin–water [83] system, pointing out that on cooling there is a sudden decrease in conductivity, which in the case of emulsions marks the inversion point. M. E. Laing and J. W. McBain,[84] however, maintain that soap solutions are not emulsions and that the decrease, which they also observed, is due to the soap crystallising out in the form of curd fibres.

A detailed study of the cataphoretic mobilities of oil drops in water and weak electrolytes has been carried out by M. Mooney,[85] using "nujol," bromoform, bromonaphthalene, phenetole, and other oils. He finds that, for emulsions of ten oils in pure water, the mobility for a field of 10 volts per cm. increases with the diameter of the oil drops for the range from 0·0005 mm. to 0·4 mm. As the potential gradient varies, small drops maintain a constant mobility, but drops larger than 0·02 mm. in diameter show a slight increase for fields of 10 volts per cm. It is suggested that the electrical double layer around a drop is considerably distorted by an external electric field, so that equilibrium is established rather slowly.

Several papers which have a direct bearing on the subject of emulsions may be mentioned under this heading.

Adsorption and interfacial tension at liquid–liquid interfaces in relation to the Gibbs adsorption equation have been investigated by J. H. Mathews and A. J. Stamm.[86] By the drop-weight method (*vide* Harkins *et alii*, *J. Amer. Chem. Soc.*, 1916, **38**, 228; 1919, **41**, 499), the interfacial tensions of two binary mixtures against water

[81] *Kolloid-Z.*, 1924, **34**, 197, 280; *A.*, ii, 529, 731.
[82] *Ibid.*, p. 94; *A.*, ii, 234.
[83] *Ibid.*, 1924, **35**, 138; *A.*, ii, 728.
[84] *Ibid.*, 18; *A.*, ii, 593
[85] *Physical Review*, 1924, **23**, 396.
[86] *J. Amer. Chem. Soc.*, 1924, **46**, 1071.

were determined, using dimethylaniline and heptane, and dimethylaniline and benzene. The results obtained support Langmuir's adsorption theory. Thus, adsorption is one molecule thick up to concentrations where a complete surface layer is formed, and the molecular thicknesses and cross-sections agree with those deduced by Langmuir. When a complete interfacial layer is formed, adsorption continues and the layer thickens.

E. M. Johansen [87] employed the drop-weight method to determine the interfacial tension between petroleum products and water. Rise of temperature lowers this tension, whilst organic acids and other impurities exert a marked depressing influence on it.

The work of Donnan (*Z. physikal. Chem.*, 1899, **31**, 42; *Kolloid-Z.*, 1910, **4**, 208) on adsorption, interfacial tension, and emulsifying efficiency in the case of oils and the sodium salts of the saturated fatty acids has been verified by R. Dubrisay and P. Picard.[88] The colloidal phenomena starting with lauric acid have been followed for higher homologues and found to be more pronounced as the molecular weight increases. Later work by Dubrisay [89] deals with the capillary phenomena which are manifested at a benzene–water interface in the presence of fatty acids and alkalis. From lauric to stearic acid, the surface energy increases with rise in molecular weight, but failure of the rule begins with arachidic acid.

Soaps.

Two papers of great importance in this field have appeared from the Bristol laboratory. M. E. Laing [90] has given a detailed study of migration, electrophoresis, and electro-osmosis of sodium oleate in an attempt to demonstrate the fundamental similarity between various processes of electrolytic conduction. J. W. McBain [91] follows this paper with one on the conception and properties of the electrical double layer and its relation to ionic migration.

From extensive experiments on the electrolytic migration of the constituents in solutions of sodium oleate (as sol, gel, and curd) Laing concludes that electrolytic migration, cataphoresis, and electrical endosmosis are strictly identical. A general formula is given, $n_1 = c_1 m_1 f_1/u$, where n_1 = the Hittorf migration number, c_1 = number of chemical equivalents per kilo. of solvent, m_1 = number of chemical equivalents which carry one electric charge, f_1 = conductivity in reciprocal ohms of one chemical equivalent,

[87] *J. Ind. Eng. Chem.*, 1924, **16**, 132.

[88] *Compt. rend.*, 1924, **178**, 205.

[89] *Ibid.*, p. 1976.

[90] *J. Physical Chem.*, 1924, **28**, 673; compare G. W. F. Holroyd and J. E. W. Rhodes on "The Electrolysis of Potassium Oleate," *J.*, 1924, **125**, 438.

[91] *J. Physical Chem.*, 1924, **28**, 706; *A.*, ii, 594.

and u = total conductivity (*i.e.*, the sum of the concentration of each conducting constituent multiplied by its mobility). This formula expresses the actual movement relative to the solvent of each constituent of any electrically conducting system (homogeneous or heterogeneous), electrolytic, colloidal, or involving double layers or diaphragms. The only distinction between colloid and crystalloid is the number of chemical equivalents which are associated with one electrical charge.

It is shown that "the relative movement of soap and water is independent of whether the soap is moving as particles of jelly or as one mass of jelly or whether the water is forced through the soap jelly, and the same value is obtained when the jelly is completely transformed into a fluid ordinary sol. . . . Whereas in dilute solution the migration of sodium oleate is that of an electrolyte, in the more concentrated solutions rather more sodium is moved towards the anode than towards the cathode. In a curd still more movement towards the anode is observed which may in some cases exceed five equivalents of oleate per one faraday of current." Laing finds the conducting constituents to be $Na^{\cdot}$ ion, a small amount of simple oleate ion, a highly-conducting micelle, and the slightly-charged, undissociated soap, this moving one-third times as fast as the ionic micelle and independently. Soap is hydrated in solution, there being ten moles of water for sodium oleate, thirteen for potassium oleate, and not exceeding seventeen for potassium laurate, reckoned in each case per equivalent of total soap. Full experimental details and the measurements made are recorded.

McBain, after discussing the Helmholtz double-layer as conceived by such investigators as Helmholtz, Lamb, Perrin, Freundlich, and others, points out that "the fundamental assumption in all these previous calculations has been that the charges, or rather the mobile ions, form an effectively complete sheath, shutting off the body of the liquid in the tube from the annular space of the double layer. If this be so, the bulk of the liquid must move along with the mobile ions and in a migration experiment the mobile ions would not appear to have moved perceptibly relative to the solvent." The work of Miss Laing shows this does not represent the facts in sols, gels, and curds of soap. McBain puts forward a conception of the double layer with sparsely distributed mobile ions, which apparently harmonises the existing data, including Miss Laing's data and those for absolute electrode potentials. It is suggested that only a very few of the ions in a double layer are mobile, the remainder being sessile and immovable.

A joint communication by Laing and McBain [92] deals with jellies

[92] *Kolloid-Z.*, 1924, **35**, 19; *A.*, ii, 593.

as contrasted with gels and curds. A 'jelly' is a completely transparent elastic mass, 'gels' being flocculent and gelatinous precipitates. Jellies may be obtained without marked interference with the equilibria in the solution; gels cannot. Soap solutions or jellies are not emulsoids.

The structure of soaps has been investigated by R. Zsigmondy [93] and by E. Kratz.[94] The former, on the basis of the vapour pressure–concentration diagram, believes the water in soap is enclosed in capillaries formed by the framework of fine, needle-like crystals of the soap, ultramicroscopic in two dimensions. Kratz finds that soap solutions contain crystal leaflets, needles, and threads in various aggregations and combinations.

A systematic investigation of the surface tensions of solutions of the sodium salts of fourteen saturated fatty acids (between C_1 and C_{26}) has been made by L. Lascaray.[95] The capillary activity of the soap increases as the molecular weight increases, reaching a maximum at C_{14} (sodium myristate), then decreases, being very small for C_{26} (sodium cerotate). The surface tension–concentration curve for the soaps, sodium hexoate to laurate, shows an inflection point at the concentration where sudden clearing occurs. This inflection point is connected with the electrolytic dissociation, hydrolysis, and colloidal structure of the soap solutions.

The electrical conductivity of soaps in the fused state and in ethyl, propyl, butyl, and amyl alcohols has been studied by S. S. Bhatnagar and M. Prasad.[96] The conductivity in the fused soaps is electrolytic, rise in temperature increasing the degree of dissociation. The conductivity in amyl alcohol was too low to be measured, but with the other alcohols the higher the alcohol the lower the conductivity, this agreeing with the Nernst-Thomson rule (*Z. physikal. Chem.*, 1894, **13**, 531). The equivalent conductivity of soap solutions in alcohols increases with dilution. Alcoholic soap solutions do not obey the Ostwald dilution law.

Effect of Hydrogen-ion Concentration.

That colloidal systems generally have properties intimately connected with the hydrogen-ion concentration of the medium is becoming more and more recognised. Numerous papers have appeared recently supporting this statement. The more important will be briefly mentioned.

P. Rona and F. Lipmann [97] have observed the effect of alterations

[93] *Z. physikal. Chem.*, 1924, **108**, 303; *A.*, ii, 391.
[94] *Z. deut. Oel-Fett-Ind.*, 1924, **44**, 25, 37, 49, 62.
[95] *Kolloid-Z.*, 1924, **34**, 73; *A.*, ii, 236.
[96] *Ibid.*, p. 193; *A.*, ii, 525. [97] *Biochem. Z.*, 1924, **147**, 163; *A.*, ii, 596.

in hydrogen-ion concentration on the precipitation of positive and negative ferric hydroxide sols. As the p_H value increases, the positively charged sol becomes more sensitive to the coagulating action of anions. The anionic series (unaffected by the p_H value) is (Br, NO_3, Cl)$<$CNS$<$F$<$$SO_4$$<$ citrate.

F. Demuth [98] finds an optimum p_H value (about 4·5) for the rapid precipitation of the casein of human milk, in the presence of suitable buffer mixtures.

The important tests based on the interaction between spinal fluid and colloidal benzoin or colloidal gold solutions depend on the p_H value. L. W. Shaffer [99] reports that the factors affecting the zone of precipitation are the alkalinity of the spinal fluid, its dilution, and the p_H of the reagent colloid.

The influence of hydrogen-ion concentration on the growth of certain bacterial plant parasites and saprophytes has been studied by E. M. Berridge,[1] whilst H. Leffmann [2] has given a summary of the work done on the relation of hydrogen-ion concentration to animal and plant growth, body fluids, etc.

Several papers deal with p_H values in relation to tanning. When benzoquinone combines with hide substance to form leather, the rate of tanning is a function of the p_H value of the solution, the maximum being at p_H 8—10.[3] Similarly, when defatted hide powder is tanned by means of gallotannic acid, the minimum rate of tanning is in the region of the isoelectric point of collagen ($p_H = 5$).[4] Data are given to show that tannin fixation at and upon the acid side of the isoelectric point of collagen is of lower degree of tenacity than that on the alkaline side.[5] H. B. Merrill [6] has shown that, in alkaline solution, hair is more readily hydrolysed than skin, the reverse being true in acid solution.

The effect of hydrogen-ion concentration has been investigated in connexion with clays,[7] adsorption of dyes,[8] colloid properties of soils,[9] and the use of gelatin in the electrolysis of inorganic salt solutions.[10]

[98] *Biochem. Z.*, 1924, **150**, 144; *A.*, i, 1134.
[99] *J. Lab. Clin. Med.*, 1924, **9**, 757.
[1] *Ann. Appl. Biol.*, 1924, **11**, 73.
[2] *J. Franklin Inst.*, 1924, **197**, 741.
[3] A. W. Thomas and M. W. Kelly, *J. Ind. Eng. Chem.*, 1924, **16**, 925.
[4] *Idem, ibid.*, p. 800. [5] *Loc. cit.*, p. 31. [6] *Ibid.*, p. 1144.
[7] R. Bradfield, *J. Physical Chem.*, 1924, **28**, 170; *A.*, ii, 237.
[8] R. E. Marker and N. E. Gordon, *J. Ind. Eng. Chem.*, 1924, **16**, 1186.
[9] R. Bradfield, *Soil Science*, 1924, **17**, 411.
[10] P. K. Frohlich, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 153; *A.*, ii, 728.

Proteins.

D. M. Greenberg and C. L. A. Schmidt [11] have published three papers: Studies on the formation and ionisation of the compounds of casein with alkali. (i) The transport numbers of alkali caseinate solutions; (ii) the conductivities of alkali caseinate solutions; (iii) the electrochemical behaviour of racemic casein.

The deposition of casein on a platinum anode occurring when direct current passes through solutions of alkali caseinates was studied quantitatively, and showed that the deposition obeys Faraday's law; also the amount of casein deposited is inversely proportional (within the limits studied) to the amount of alkali combined with the protein. The bases used were cæsium, potassium, sodium, and rubidium hydroxides. The mobility of casein ion calculated from the transference numbers at 30° varied somewhat with the nature of the kation, but was surprisingly high, from 43·0 to 46·5 mhos. The authors discuss the high value of this mobility in relation to McBain's theory of colloidal electrolytes (J. W. McBain and C. S. Salmon, *J. Amer. Chem. Soc.*, 1920, **43**, 426). The temperature gradient of the casein-ion mobility was determined as 3 mhos per degree centigrade (as against 1·05 mhos for $Na^{\cdot}$, 1·32 mhos for $K^{\cdot}$, and 1·44 mhos for $Cs^{\cdot}$). Just as McBain found a high conductivity temperature coefficient in soap solutions, which he explains by assuming a dehydration of the complex soap micelle, so probably does dehydration occur in protein solutions, the viscosity then decreasing as the temperature rises.

Greenberg and Schmidt sum up by stating that they believe casein ions and inorganic kations are present in the solutions and act as the carriers of the electric current.

The physical chemistry of casein has been investigated in considerable detail by E. J. Cohn, R. E. L. Berggren, and J. L. Hendry,[12] in a study of the amino-acid composition of casein and its capacity to combine with base. The coagulation of casein from calcium caseinate solutions by means of hydrochloric acid and its relation to hydrogen-ion concentration have been dealt with by F. Loebenstein.[13]

Several papers relating to gelatin are of importance. The isoelectric point of pure hide gelatin has been found to be at p_H 5·5, that of bone gelatin being less than p_H 5·0.[14] D. J. Hitchcock [15] finds that gelatin at 40° retains its isoelectric point at about p_H 4·7. This is deduced from his measurements of the osmotic pressure and

[11] *J. Gen. Physiol.*, 1924, **7**, 287, 303, 317.
[12] *Ibid.*, p. 45. [13] *Kolloid-Z.*, 1924, **34**, 227.
[14] O. Gerngross, *J. Amer. Leath. Chem. Assoc.*, 1924, **19**, 258.
[15] *J. Gen. Physiol.*, 1924, **6**, 456; *A.*, ii, 460.

viscosity of 1% gelatin solutions (at 40°) containing varying amounts of hydrochloric acid or sodium hydroxide.

The equivalent weight of gelatin is given as 1180 by W. R. Atkin and G. W. Douglas,[16] from p_H values resulting when standard hydrochloric acid or sodium hydroxide was added to 1% solutions of isoelectric gelatin. The titration curve apparently consists of four portions, p_H 1·7—4·7, p_H 4·7—7·7, p_H 7·7—12·6. The significance of these definite p_H regions is dealt with.

The value of the molecular or equivalent aggregate weight of gelatin as found by R. Wintgen and H. Löwenthal [17] is about 30,000. The method employed depends on the reciprocal precipitation of gelatin and chromic oxide hydrosols.

The dissolution of gelatin on standing in contact with water or dilute acids or alkalis at the ordinary temperature has been studied by F. Fairbrother,[18] who suggests that the framework of a gelatin gel consists of isoelectric gelatin and gelatin kations.

F. E. Brown [19] has criticised the work of Svedberg and Stein (*A.*, i, 104) on density and hydration in gelatin sols. He disputes the conclusion that density changes are due to the formation of a shell of highly compressed water around the gelatin particle. Svedberg [20] accepted Brown's criticism and agreed the measurements made were insufficient on which to base conclusions regarding the hydration of gelatin. Further experiments have now been made on the swelling and dissolution of gelatin in water and under the influence of acids and alkalis, neutral salts and non-electrolytes.

W. G. France and W. H. Moran [21] have studied the influence of gelatin on the transference numbers of hydrochloric acid. They considered that their results support the view that gelatin reacts with acids to form an adsorption complex or additive chemical compound which dissociates. G. Scatchard [22] criticises this work and shows that the theoretical and the experimental treatment of the problem are much more complicated than France and Moran believe. He finds no evidence in their paper to support the view outlined, whereas other workers (Loeb and Hitchcock) have experimental support of it.

Determinations of the surface tension of gelatin solutions have been carried out in relation to concentration, p_H, and temperature.[23] A transition point was evidenced at 38°. As the gelatin concentration

[16] *J. Soc. Leather Trades Chem.*, 1924, **8**, 359; *A.*, ii, 592.
[17] *Kolloid-Z.*, 1924, **34**, 289; *A.*, ii, 739.
[18] *Biochem. J.*, 1924, **18**, 647; *A.*, ii, 592.
[19] *J. Amer. Chem. Soc.*, 1924, **46**, 1207; *A.*, ii, 660.
[20] *Ibid.*, p. 2673. [21] *Ibid.*, p. 19. [22] *Ibid.*, p. 2353.
[23] C. E. Davis, H. M. Salisbury, and M. T. Harvey, *J. Ind. Eng. Chem.*, 1924, **16**, 161; *A.*, ii, 235.

is increased, surface tension diminishes. With the more concentrated gelatin solutions, rise in temperature raises surface tension, reaching a maximum; the surface tension now decreases as the temperature approaches the transition point. Above this temperature, the surface tension remains nearly constant. With increasing p_H values, gelatin solutions of all concentrations point to a maximum surface tension at the neutral point.

H. P. Higley and J. H. Mathews [24] have investigated, by a spectrophotometric method, the relationship between the wave-length of maximum absorption in the ultra-violet and the p_H values of 1% gelatin solutions. The results are given in the form of curves in which p_H values are abscissæ and the ordinates are wave-lengths for definite fractions of light absorbed, the fraction being 0·75, 0·6, 0·4, and 0 (transparent). There is a sharp shift of the absorption band toward the ultra-violet as the p_H values of 4·69 and 7·65 are approached. The first value is about the accepted isoelectric point for gelatin, whilst p_H 7·65 is close to the value given by Wilson and Kern for the minimum swelling of gelatin. Two points of maxima are shown at about p_H 3·7 and p_H 6·6, which values agree with those found by Loeb and G. Wilson and Kern respectively.

An important paper by N. D. Scott and The Svedberg [25] concerns the measurement of the mobility of egg-albumin at different acidities. The cataphoretic position of the protein layer was determined by photographing the fluorescence when illuminated by ultra-violet light. The authors believe their measurements to be "practically the first direct quantitative measurements of the mobility of a natural protein." Buffer mixtures of sodium acetate with acetic acid and of disodium hydrogen phosphate with citric acid were used over a range of p_H from 7 down to about 3 and 2·5, respectively. Mobility is most intimately related to p_H, and the maximum mobility observed was toward the cathode, $21·79 \times 10^{-5}$ cm. per second at a p_H of 2·93.

Membrane Equilibria.

An interesting essay on "The Theory of Membrane Equilibria" has been published by F. G. Donnan,[26] who surveys the work of his collaborators and also the views of Loeb and Proctor and Wilson. Donnan emphasises that the theory of membrane equilibria depends simply on the assumption of the existence of equilibrium, and the existence of certain constraints restricting the diffusion of one or more electrically charged or ionised constituents. The simple mathematics of the Donnan equilibrium are given for various

[24] *J. Amer. Chem. Soc.*, 1924, **46**, 852; *A.*, ii, 460.
[25] *Ibid.*, p. 2700.
[26] *Chemical Reviews*, 1924, **1**, 73

possible cases. Fair agreement between theory and experiment has recently been found in the study of the equilibrium between sodium caseinate and potassium caseinate across a membrane of parchment paper; also in the case of sodium caseinate and sodium chloride.

J. Loeb [27] has investigated the influence of electrolytes on membrane potentials and cataphoretic potentials. The active ion in the depressing action of electrolytes on membrane potentials as well as on cataphoretic potentials has the opposite sign of charge to that of the colloidal particle. Only the valency, not the chemical nature, of the active ion determines this depressing effect, as now proved with suspensions of collodion, mastic, Acheson's graphite, and denatured egg-albumin. The influence of dilute acids on the cataphoretic *P.D.* of gelatin-coated collodion particles depends only on the p_H value and the valency rule. Observation of the depressing effects of salts with univalent and bivalent kations on the cataphoretic *P.D.* of collodion led Loeb to conclude with Wilson ("The Chemistry of Leather Manufacture," New York, 1923, p. 128) that the cataphoretic *P.D.* between particles and an aqueous solution (no chemical changes taking place) is due to a Donnan equilibrium between the film which adheres to and moves with the particles in cataphoresis and the oppositely charged film of the double layer. The film moving with the particle has (in, for example, gold particles in sodium chloride solution) an excess of kations, whilst the other film of the double layer has a corresponding excess of anions.

An inquiry into the molecular nature of the ultimate particles in protein solutions has been made by J. Loeb and M. Kunitz,[28] using a viscosimetric method, on the view that the viscosity of such suspensions as casein in hydrochloric or orthophosphoric acid is due to the aggregation of protein particles, which swell in accordance with the Donnan equilibrium. The experimental results obtained were used to ascertain whether the ultimate units of genuine protein in *solutions* are aggregates large enough to give rise to a Donnan equilibrium, or whether they consist of particles below this limit, and in what ratio the two kinds of units occur in the solution. Thus when 1 g. of isoelectric casein is dissolved in hydrochloric acid, the final solution being at $p_H = 2{\cdot}45$, more than 0·5 g. of casein exists in the form of particles too small to give rise to the Donnan equilibrium, but the rest are still capable of swelling in acid.

M. Kunitz [29] has made a detailed study on the influence of salts on those physicochemical properties of sodium gelatinate which are regulated by the Donnan equilibrium, *viz.*, osmotic pressure, mem-

[27] *J. Gen. Physiol.*, 1924, **6**, 307; *A.*, ii, 310.
[28] *Ibid.*, p. 479; *A.*, ii, 460.
[29] *Ibid.*, p. 547; *A.*, ii, 461.

brane potential, and swelling. The results obeyed the same valency rules as in the case of the influence of salts on gelatin chloride (*loc. cit.*, 1922—23, **5**, 665, 693). The rules state that, when a salt is added to an ionised protein without causing a change in p_H of the protein, the general effect is a depression of the mentioned properties. The degree of depression depends, not only on the concentration of the salt, but also on the electrical properties of the ions of the salt. Of the two or more oppositely charged ions of which a salt consists, only the valency of those ions which carry charges of opposite sign to those carried by the protein ions affects the degree of dispersion, which increases with the valency of the ions.

Donnan's theory is supported by experiments on the ion activity ratios for the inside and outside of gelatin particles. *E.M.F.* measurements were made by J. H. Northrop and M. Kunitz.[30] The ratios of the total concentrations of calcium, magnesium, potassium, and zinc do not agree with the calculated ratios, probably because of the formation of complex ions with the protein. Since protein combines less readily with chlorine than with zinc, the addition of zinc chloride to isoelectric protein should give rise to an unequal distribution. That this is the case was shown by an increase in swelling, osmotic pressure, and viscosity.

The relation between membrane equilibria and the electric charge of red blood-cells has been investigated by C. B. Coulter,[31] who finds that the Donnan equilibrium determines the distribution of hydrogen- and chlorine-ions between the cell and the surrounding fluid. The distribution of the HPO_4'' ion, however, appears to be mainly influenced by the relative impermeability of the cell membrane to this anion.

C. D. Murray [32] has described a system consisting of two aqueous solutions containing equal concentrations of lactic acid, but different concentrations of sodium lactate, separated by a layer of amyl alcohol. The amyl alcohol acts as a semipermeable membrane and is relatively impermeable to sodium ions, which here play the *rôle* of the protein ions often used in similar studies with collodion membranes. As the concentration of sodium lactate increased, electrical properties were exhibited ranging from those characteristic of a simple Donnan equilibrium to those characteristic of simple diffusion. Murray emphasises the fact that the Donnan *P.D.* can be treated as a special case of a diffusion potential.

Confirmation of Donnan's theory of membrane equilibrium has been obtained by N. Bjerrum,[33] working with an exceedingly stable sol of chromium hydroxide. This was contained in a collodion

[30] *J. Gen. Physiol.*, 1924, **7**, 25; *A.*, ii, 831. [31] *Ibid.*, p. 1; *A.*, ii, 835.
[32] *Ibid.*, 1924, **6**, 759; *A.*, ii, 744. [33] *Z. physikal. Chem.*, 1924, **110**, 656.

membrane, bathed by solutions of various electrolytes, and measurements were made of osmotic pressure, membrane *P.D.*, and p_H value. For colloidal ions with constant electric charge, Bjerrum deduces the relation that the osmotic pressure due to the colloidal particles themselves is independent of the concentration of electrolytes and proportional to the chromium concentration. On the other hand, the osmotic pressure resulting from the Donnan membrane equilibrium varies inversely as the concentration of electrolytes and directly as the square of the chromium concentration.

E. B. R. Prideaux and W. E. Crooks [34] have published the results of an investigation on the diffusion potentials and ionic mobilities of benzoates and salicylates, and their modification by a membrane of parchment paper. This paper is interesting, since a true semi-permeable membrane is not used, so that both ions can pass, although the slower ion is proportionately more impeded.

Periodic Precipitation and the Liesegang Phenomenon.

A number of authors propose new theories of the Liesegang phenomenon. R. Fricke [35] concludes that the ordinary diffusion equations, suitably modified to allow for the removal of solute by precipitation, combined with the assumption of a metastable limit, adequately explain the occurrence of rhythmic precipitation, and even details of the conditions in which they are formed. Experimental results with a number of reactions are given. K. C. Sen and N. R. Dhar [36] dispute the conclusion drawn by A. M. Williams and M. R. Mackenzie [37] that silver chromate diffuses as a crystalloid, and assume the formation of a silver chromate sol by peptisation and the periodic coagulation of this sol. J. Traube and K. Takehara [38] give a rough sketch of yet another explanation, which is based on experiments by the latter [39] on precipitation in gelatin sols. The variations in the colour and dispersity of the precipitate, caused by varying concentrations of the reaction components, are supposed to occur also in the gel, when the same concentrations are established; no experimental evidence of the correctness of this assumption is, however, given.

C. A. Schleussner [40] investigates the distance between the silver chromate rings of the original Liesegang experiment and confirms the result that they increase in geometrical progression. This law applies also to the "intermediate" rings separated by microscopic intervals. H. Handovsky and E. du Bois-Reymond [41] obtain

[34] *Trans. Faraday Soc.*, 1924, **20**, 37.
[35] *Z. physikal. Chem.*, 1924, **107**, 41.
[36] *Kolloid-Z.*, 1924, **34**, 270.
[37] *J.*, 1920, **117**, 844.
[38] *Kolloid-Z.*, 1924, **35**, 245.
[39] *Ibid.*, p. 233.
[40] *Ibid.*, p. 338.
[41] *Ibid.*, **33**, 347.

rings by allowing alkaloid solutions to diffuse into gelatin containing iodine in potassium iodide. S. S. Bhatnagar and K. K. Mathur [42] draw a parallel between Liesegang rings and the concentric rings of vesicles in *Herpes tonsurans*, with the suggestion that the latter are caused by acid produced by the micro-organism. M. Watanabe,[43] in a study of diffusion problems in reference to ore deposits, gives particulars of numerous periodic precipitations, chiefly of hydroxides and sulphides.

Various authors describe stratifications obtained in the absence of gels. J. Brodersen [44] produces them by allowing sodium chloride solution to diffuse into silver nitrate solution contained in the capillary space between two cover-glasses. The number of strata increases with decreasing depth of the space. P. D. Zacharias [45] describes a periodic deposit formed on the wall of a bottle containing a natural mineral water and consisting largely of clay, with organic matter and very little sulphur. A. Janek [46] places a crystal of silver nitrate, covered with a drop of water, on dichromate-gelatin: the drop is gradually covered with a banded membrane of silver chromate, which grows from the periphery towards the centre.

Gels.

A. Szegvari [47] describes a sol of cellulose nitrate in amyl acetate–light petroleum, which gelates reversibly on heating. The viscosity of the sol and its tendency to gelate do not run parallel. R. Reiger,[48] in a long mathematical paper on the kinetics of gelation, discusses the change in optical rotation with time. Above a certain temperature, rotation is independent of time; at lower temperatures, it increases with time, and this change is held to prove molecular rearrangement. Careful examination of the time–rotation curves shows that the change proceeds by steps, each of which is of the simplest type, *viz.*, monomolecular. The differential equations for the assumed series of steps are developed and integrated. Graphs for the change in rotation at 25° during 120 minutes show two breaks. The other methods of studying gelation, *viz.*, time–viscosity and time–elasticity curves, are then discussed, and both, when carefully plotted, show the discontinuities required by the theory. Sh. Dokan deals with the effects of electrolytes on the swelling of agar [49] and of "konyaku," [50] the starch of "a tuber resembling the potato" gelatinised by alkali and sold, as a common article of food, in sheets

[42] *Kolloid-Z.*, 1924, **34**, 104.
[43] *Sci. Rep. Tôhoku Imp. Univ.*, Ser. 3, Vol. 2, Nos. 1 and 2.
[44] *Kolloid-Z.*, 1924, **35**, 21.
[45] *Ibid.*, **34**, 38. [46] *Ibid.*, **33**, 86. [47] *Ibid.*, **34**, 34.
[48] *Koll. Chem. Beihefte*, 1924, **19**, 381.
[49] *Kolloid-Z.*, 1924, **34**, 155. [50] *Ibid.*, **35**, 11.

resembling gelatin. The swelling of agar is depressed by *all salts*. The p_H of the solution is of very little influence up to about 5·0. With low concentrations of salts, the effect is due entirely to the kation, and the depression of swelling increases with increasing valency. Hydrogen ion is anomalous and depresses swelling even more than aluminium ion. With concentrations higher than 0·01*N*, the specific effects of the ions appear, and the anions group themselves in the order of the normal Hofmeister series. The effects on konyaku differ considerably from those on agar. Chlorides in concentration below 0·1*N* have no effect; in higher concentrations, the kations on the whole follow the ordinary lyotropic order. Hydrogen ion does not occupy an exceptional position. No well-defined equilibrium is attained in swelling, as peptisation occurs *pari passu*. Peptisation takes place in 24 hours with concentrations of the order 1·0*N*; the stronger the swelling, the more marked is peptisation. The viscosity of the sols is unaffected by electrolyte concentrations below 0·1*N*; in higher concentrations, the surprising result appears that the more a given ion *promotes* swelling the more it *depresses* the viscosity. Hydroxyl ion occupies an exceptional position and reduces viscosity already in low concentrations.

G. Wendelmuth [51] studies the gelation of fruit juices and of sols of pure pectin prepared from the endocarp of oranges and lemons. The theoretical conclusions drawn are: the tendency to gelate is reduced by purification and by ageing; the viscosity of the dilute boiled mixtures of fruit juice and sugar is parallel with the strength of the finished jelly; the effects of sugar content, pectin concentration and p_H can be estimated quantitatively; gelation is not simply a function of temperature or electrolyte concentration, as jellies equal to those obtained by boiling can be prepared by stirring fruit juice with sugar in the cold. The sugar acts chiefly as a dehydrating agent. The effect of calcium chloride on acid–sugar–pectin gels has been investigated by E. G. Halliday and G. B. Bailey.[52] The percentage of pectin, acid, and sugar used for a standard jelly were each in turn lowered to a point where an acceptable jelly failed to form in a given time. To these non-jelling mixtures, calcium chloride was added and in every case gelation took place. Additions above 0·5—1·0% were without further effect, but promoted syneresis. S. E. Sheppard and S. S. Sweet [53] examine the connexion between the empirical jelly strength figures obtained with various testers and the elastic constants of gelatin gels. The apparent jelly strength is a function of the size of the test piece; elongation tests show

[51] *Koll. Chem. Beihefte*, 1924, **19**, 115.
[52] *J. Ind. Eng. Chem.*, 1924, **16**, 595.
[53] *Ibid.*, p. 593.

apparently high elasticity for shorter test pieces. Poisson's ratio is found to be 1/2, *i.e.*, the gel volume remains unaltered by deformation, which is in agreement with the results of previous observers. R. Schwarz and Fr. Stöwener [54] investigate the ageing of silicic acid gels by studying the solubility in ammonia and the conductivity of the resulting solutions. They conclude that ageing is due to dehydration of primary particles originally associated with much water.

Adsorption.

A large number of papers have been published during 1924 on the subject of adsorption. The great activity in this field is due not only to the wealth of theoretical problems available, but also to the increasing technical applications of the data secured.

The theory of adsorption has been dealt with by several workers. B. Iliin [55] considers the electrical nature of adsorption forces and deduces a relation between the adsorption capacity and the dielectric constant of the adsorbed gel. W. Tarassoff,[56] working on similar lines, shows that the heat of adsorption should be proportional to $(\epsilon - 1)/\epsilon$, where ϵ is the dielectric constant of the adsorbed gas. The adsorption of gases by solids has been examined by J. Frenkel [57] from a kinetic point of view. The theory of ionic adsorption has been studied by A. Gyemant,[58] his equations being developed thermodynamically and involving the electrokinetic potential ζ, as distinct from the thermodynamic potential, E. F. E. Bartell and E. Miller [59] extend Langmuir and Harkins's theory of adsorption and orientation at interfaces to their work on charcoal as adsorbent in water and solutions. The origin of the electrical double layer is discussed as a case of orientation of adsorbed ions.

A series of papers on adsorption has been published by P. N. Pavlov.[60] His third paper, on the surface tension of liquid mixtures and adsorption, is a mathematical one, and deals incidentally with the limitations of the Gibbs equation, which should not be applied to adsorption from solutions. All the papers are theoretical and partly mathematical, and experimental data are given in support of the equations deduced.

Adsorption at a liquid–gas interface has been studied by T. Iredale,[61] using mercury drops for the adsorption of gas or vapour.

[54] *Koll. Chem. Beihefte*, 1924, **19**, 171.
[55] *Phil. Mag.*, 1924, [vi], **48**, 193; *A.*, ii, 663.
[56] *Physikal. Z.*, 1924, **25**, 369; *A.*, ii, 733.
[57] *Z. Physik*, 1924, **26**, 117.
[58] *Z. physikal. Chem.*, 1924, **108**, 387; *A.*, ii, 391.
[59] *J. Physical Chem.*, 1924, **28**, 992; *A.*, ii, 734.
[60] *Kolloid-Z.*, 1924, **35**, 3, 87, 89, 156, 159, 221, 375; *A.*, ii, 732–733.
[61] *Phil. Mag.*, 1924, [vi], **48**, 177; *A.*, ii, 663.

Adsorption lowered the surface tension of the mercury and diminished the size of the drops. At saturation pressure there is a sudden fall in the surface tension and a liquid film forms on the drop. A. Frumkin [62] investigated the adsorption of inorganic electrolytes from solution at the air–liquid boundary by an electrometric method and obtained results agreeing with the usual surface tension measurements. Thus salts which exerted the greatest charge at the liquid surface increased the surface tension of the water the least. A detailed study of foams has been made by O. Bartsch,[63] whilst E. K. Rideal and C. G. L. Wolf [64] have investigated the well-known chemical destruction of rennin solutions on agitation. Agitation causes frothing and an increase in the air–liquid interface. A chemical reaction takes place at this interface between capillary active rennin and a capillary active substance present in ordinary rennin solutions.

Adsorption at a solid–gas interface has been studied by several workers, mainly using charcoal :—

(*a*) R. Lorenz and E. Wiedebrauck [65]—Adsorption of oxygen, nitrogen, hydrogen, and carbon dioxide from known mixtures. Increase in the rate of flow of the gas was found to increase the time required to attain equilibrium.

(*b*) G. Sameshima and K. Hayashi [66]—Adsorption of air by different varieties of charcoal, at temperatures from — 185° to the ordinary temperature. Coconut charcoal has the greatest adsorptive capacity by volume, but is not much different from other charcoals on a weight basis.

(*c*) O. Ruff and E. Hohlfeld [67]—The effect of temperature and the nature and rate of passage of activating gases on charcoal activity.

(*d*) A. S. Coolidge [68]—Adsorption at 0° to 300° and 0·0002 mm. to 1000 mm. for benzene, carbon disulphide, carbon tetrachloride, chloroform, water, etc. He concludes that the adsorbed substance exists as a liquid, even below the freezing point of the pure liquid.

(*e*) E. A. Blench and W. E. Garner [69]—Determination of the heat of adsorption of oxygen by charcoal. They found that "the heat of adsorption of oxygen by charcoal for the first small quantities of oxygen adsorbed ranges from 60 to 220 cal./mol. of oxygen adsorbed as the temperature of adsorption rises from 18° to 450°, and falls off rapidly as the surface becomes saturated."

[62] *Z. physikal. Chem.*, 1924, **109**, 34; *A.*, ii, 462.
[63] *Koll. Chem. Beihefte*, 1924, **20**, 1.
[64] *Proc. Roy. Soc.*, 1924, [*A*], **106**, 97.
[65] *Z. anorg. Chem.*, 1924, **135**, 42.
[66] *Sci. Rep. Tôhoku Imp. Univ.*, 1924, **12**, 289.
[67] *Kolloid-Z.*, 1924, **34**, 135. [68] *J. Amer. Chem. Soc.*, 1924, **46**, 596.
[69] *J.*, 1924, **125**, 1288.

E. C. Williams [70] has an important paper dealing with silica gel as an industrial adsorbent, whilst D. H. Bangham and F. P. Burt [71] have investigated the rates of adsorption and desorption of gases by a glass surface. The sorption values all greatly exceeded the values anticipated by adsorption to unimolecular films. R. Lorenz and E. Wiedebrauck [72] describe a dynamic method for determining gas adsorption.

The heats of adsorption of gases on metallic catalysts have been measured by R. A. Beebe and H. S. Taylor.[73] The values depend on the previous history of the catalyst. For nickel adsorbing hydrogen, the heats of adsorption ranged from 13,500 to 20,500 cals. per g.-mole of hydrogen, whilst the value 9600 was found for a particularly active copper catalyst.

Considerable activity has marked the study of adsorption at a solid–liquid boundary. The properties of active charcoal are discussed by H. H. Lowry,[74] and its preparation by Philip.[75] The adsorption of binary mixtures (pair of electrolytes) by animal charcoal and the adsorptive power of different varieties of charcoal have been investigated by N. A. Yajnik and T. C. Rana.[76] E. J. Miller [77] finds evidence that hydrolytic or decomposition adsorption occurs when electrolytes are adsorbed from solution by charcoal.

The adsorption of dyes on diamond, charcoal, and artificial silk has been studied by F. Paneth and A. Radu,[78] who give evidence for the adsorption of monomolecular layers. Dyes are also adsorbed on crystals in monomolecular layers.[79] The question whether adsorption occurs as a single layer or a series of superposed layers is discussed by G. C. Schmidt and F. Duran.[80] Glass plate and powder adsorbed aniline dyes. From the data obtained, the adsorbed layer may be one or two moles deep, depending on the assumptions made as to the shape and orientation of the dye molecules.

WILLIAM CLAYTON.

[70] *J. Soc. Chem. Ind.*, 1924, **43**, 97T.
[71] *Proc. Roy. Soc.*, 1924, [*A*], **105**, 481; *A.*, ii, 392.
[72] *Z. anorg. Chem.*, 1924, **134**, 251.
[73] *J. Amer. Chem. Soc.*, 1924, **46**, 43.
[74] *Ibid.*, p. 824; *A.*, ii, 393.
[75] J. C. Philip and J. Jarman, *J. Physical Chem.*, 1924, **28**, 346; *A.*, ii, 393.
[76] *Ibid.*, p. 267; *A.*, ii, 308.
[77] *J. Amer. Chem. Soc.*, 1924, **46**, 1150; *A.*, ii, 664.
[78] *Ber.*, 1924, **57**, [*B*], 1221.
[79] F. Paneth and W. Thimann, *ibid.*, p. 1215.
[80] *Z. physikal. Chem.*, 1924, **108**, 128; *A.*, ii, 238.

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